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Supporting Information

A Triad of Highly Reduced, Linear Iron Nitrosyl Complexes: {FeNO}$^{8-10}$

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Supporting Information

Contents:

Experimental Part:

General Considerations: All manipulations were carried out using standard Schlenk or glovebox techniques under an N_2 atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thoroughly sparging with N_2 gas followed by passage through an activated alumina column in the solvent purification system by SG Water, USA LLC. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. All reagents were purchased from commercial vendors and used without further purification unless otherwise stated. [TPBFeN_2][1], and [TBA][BArF][2] were synthesized via known literature procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. C_6D_6 was degassed and stored over activated 3 Å molecular sieves prior to use, and THF-d_8 was dried with NaK and vac-transferred into a dry vessel. Elemental analysis for **{TPBFeNO}^{8}** was performed by Midwest Microlab, LLC, Indianapolis, IN, and elemental analysis for **{TPBFeNO}$^{9\text{-}10}$** was performed by the Beckman Institute Elemental Analysis facility at California Institute of Technology. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to tetramethylsilane, using residual solvent resonances as internal standards. ^{31}P NMR chemical shifts are reported in ppm relative to 85% aqueous H_3PO_4. ^{11}B NMR chemical shifts are reported in ppm relative to a 15% solution of $BF_3{\cdot}OEt_2$ in $CDCl_3$ Solution phase magnetic measurements were performed by the method of Evans.[3] Solid IR measurements were obtained on a Bruker Alpha spectrometer equipped with a diamond ATR probe.

EPR Spectroscopy: X-band EPR spectra were obtained on a Bruker EMX spectrometer on 2-5 mM solutions prepared as frozen glasses in 2-methyltetrahydrofuran (2-MeTHF). Samples were collected at powers ranging from 20 μW to 15 mW and modulation amplitudes of 1-5 Gauss. Spectra were simulated using the EasySpin[4] suite of programs with Matlab 2013.

Optical Spectroscopy: Measurements were taken on a Cary 50 UV/Visible spectrophotometer using a 1 cm quartz cell connected to a round-bottom flask and sealed with a Teflon stopcock. Variable temperature measurements were collected with a Unisoku CoolSpek cryostat mounted within the Cary spectrophotometer. Density corrections were applied using literature temperature vs. density data available for 2-MeTHF.[5]

X-Ray Crystallography: XRD studies were carried out at the Beckman Institute Crystallography Facility on a Brüker Kappa Apex II diffractometer (Mo Kα radiation). Structures were solved using SHELXS or SHELXT and refined against F^2 on all data by full-matrix least squares with SHELXL.[6] The crystals were mounted on a glass fiber under Paratone N oil.

Electrochemistry: Electrochemical measurements were carried out in a thick-walled one-component electrochemical cell fitted with a Teflon stopcock and tungsten leads protruding from the top of apparatus. A CD instruments 600B electrochemical analyzer was used for data collection. A freshly-polished glassy carbon electrode was used as the working electrode, a platinum wire was used as the auxiliary electrode, and a silver wire as a reference electrode. The analyte was used in 1 mM concentration. After the desired scans were completed, ferrocene (1 mM) was added to serve as an internal reference. All reported potentials are referenced to the ferrocene couple, Fc/Fc^+.

^{57}Fe Mössbauer Spectroscopy: Spectra were recorded on a spectrometer from SEE Co (Edina, MN) operating in the constant acceleration mode in a transmission geometry. The sample was kept in an SVT-400 cryostat from Janis (Wilmington, MA). The quoted isomer shifts are relative to the centroid of the spectrum of a metallic foil of α-Fe at room temperature. Solid samples were prepared by grinding crystalline material and then mounted in a Delrin cup fitted with a screw-cap as a boron nitride pellet. Data analysis was performed using the program WMOSS (www.wmoss.org) and quadrupole doublets were fit to Lorentzian lineshapes except where noted.

Calculations: Optimizations were performed using the ORCA program.[7] Frequency calculations were performed using the Gaussian 09 program.[7] Gas-phase structures were optimized using the crystal structure coordinates as the input. The BP86[9] and B3LYP[10] functional with the 6-31G(d) basis set was used on C and H,[11] and the def2-TZVPP basis set was used on P, B, Fe, N, and O.[12] That optimized structures represented true stationary points was checked by doing a single-point frequency calculations on the optimized structure, which in all cases revealed no negative frequencies or one negative frequency that was small ($\geq$ -30 cm^{-1}) and weak. Bond indices were calculated using the built-in Wiberg Bond Index algorithm in Gaussian 09. Broken symmetry solutions were found by first optimizing the high spin wavefunction and then using the Flip Spin keyword in ORCA to find and optimize a broken symmetry solution. Mössbauer parameters were calculated by doing a single point calculation on the BP86 optimized structure using TPSSH[13] and CP(PPP) on Fe;[14] def2-TZVP on P, B, and N;[12] and def2-SVP on C and H.[15] The obtained density was converted to an isomer shift using the calibration constant obtained by Neese and coworkers for this functional.[16]

Synthetic Procedures:

{TPBFeNO}^{8}-A vial containing [NO][PF_6] (11.4 mg, 0.065 mmol, 1.0 eq.) and a stir bar was chilled to -78 °C. A suspension of TPBFeN_2 (45.0 mg, 0.067 mmol, 1.02 eq.) in DME (3 mL) was chilled to -78 °C. Using a syringe the suspension of TPBFeN_2 was added in one portion to the stirring [NO][PF_6]. This mixture was then immediately capped and allowed to stir at -78 °C for a half hour before being warmed to room temperature. It was then stirred at room temperature for an additional half hour to yield a black solution. The solvent was removed under reduced pressure, and the oily solid was washed with pentane (3 x 1 mL), ether (3 x 1 mL) and benzene (3 x 1 mL). The residual solid was dissolved in THF and filtered through celite. The THF solution was then layered with benzene, and precipitated by slow diffusion of pentane overnight. This yielded crystalline purple material of [TPBFeNO][PF_6] (not characterized due to its very poor solubility after recrystallization) which was then suspended in Et_2O (2 mL) and stirred with NaBArF (0.95 eq.) overnight. The ether was then filtered to remove salts and the solvent was removed in vacuo. The purple solid is then dissolved in minimal THF and pentane was allowed to diffuse in overnight yielding purple crystals of **{TPBFeNO}^{8}** (yield = 41.1 mg, 41%).
^{1}H NMR (RT, THF-d_8, 400 MHz): δ = 7.80 (11 H, br s, Ar-*H*), 7.68-7.48 (10 H, m, Ar-*H*), 7.27 (3 H, d, ^{3}J(H-H) = 7.2 Hz, Ar-*H*), 2.86 (3 H, m, PC*H*), 1.73 (9 H, m), 1.58 (9 H, 'dd' ^{4}J(P-H) = 14.5 Hz and ^{3}J(H-H) = 7.0 Hz, PCHCH_3), 1.02 (9 H, 'dd' ^{4}J(P-H) = 14.5 Hz and ^{3}J(H-H) = 6.3 Hz, PCHCH_3), 0.81 (3 H, br s, PC*H*), 0.71 (9 H, 'dd' ^{4}J(P-H) = 12.0 Hz and ^{3}J(H-H) = 6.4 Hz, PCHCH_3).

^{1}H NMR (-78 °C, THF-d_8, 500 MHz): δ = 8.17 (2 H, 't' ^{3}J(H-H) = 8.9 Hz, Ar-*H*), 7.99 (2 H, br s, Ar-*H*), 7.90 (8 H, s, BArF-*H*), 7.74 (4 H, s, BArF-*H*), 7.54 (2 H, br s, Ar-*H*), 7.49 (2 H, br s, Ar-*H*), 7.34 (2 H, br s, Ar-*H*), 7.30 (1 H, br s, Ar-*H*), 6.88 (1 H, br s, Ar-*H*), 3.62 (1 H, br s, PC*H*), 3.41 (1 H, br s, PC*H*), 3.06 (1 H, br s, PC*H*), 2.33 (1 H, br s, PC*H*), 1.94 (4 H, br s, PCHCH_3), 1.89-1.77 (4 H, m, PCHCH_3), 1.60 (3 H, br s, PCHCH_3), 1.51 (3 H, br s, PCHCH_3), 1.42 (3 H, d ^{3}J(H-H) = 15.7 Hz, PCHCH_3), 1.24 (4 H, br s, PCHCH_3), 1.11 (6 H, br s, PCHCH_3), 0.86 (3 H, d ^{3}J(H-H) = 12.7 Hz, PCHCH_3), 0.55 (3 H, br s, PCHCH_3), .47 (3 H, br s, PCHCH_3), -0.07 (1 H, br s, PC*H*), -0.17 (1 H, br s, PC*H*).
^{31}P NMR (RT, THF-d_8, 162 MHz): δ = 64.0 (br).
^{31}P NMR (-78 °C, THF-d_8, 202 MHz): δ = 84.4 (br), 80.0 (br), 19.6 (br).
^{11}B NMR (RT, THF-d_8, 128 MHz): δ = 36.7 (br, TPB), -2.0 (sh, BArF).
^{13}C NMR (RT, THF-d_8, 100 MHz): δ = 164.8 (q, ^{2}J(C-B) = 29.7 Hz), 139.1 (br), 137.5 (s), 134.3 (d, ^{2}J(C-P) = 17.3 Hz), 133.2 (br), 131.9 (m), 127.4 (q, ^{2}J(C-F) = 72.2 Hz), 120.1 (m), 35.0 (d, ^{2}J(C-P) = 19.0 Hz), 30.6 (d, ^{2}J(C-P) = 8.9 Hz), 24.8 (d, ^{3}J(C-P) = 4.2 Hz), 24.0 (s), 23.7 (s), 21.7 (s).
^{19}F NMR (RT, THF-d_8, 376 MHz): δ = -63.4 (s).
IR (Thin Film): 1745 cm^{-1} (ν_{NO}).
UV/Vis (2-MeTHF, nm {cm^{-1} M^{-1}}): 463 {220}, 565 {350}.
Elemental Analysis: theory [C 53.05, H 4.32, N 0.91]; found [C 53.11, H 4.17, N 1.08]

{TPBFeNO}^{9}-The microcrystalline material, [TPBFeNO][PF_6], (38.0 mg, 0.046 mmol, 1.0 eq) was suspended in THF (5 mL) and added to a vial containing Cp_2Co (8.7 mg, 0.046 mmol, 1.0 eq.). The suspension was stirred for three hours during which the color of the solution lightened to an orange-pink color. The solvent was then removed under reduced pressure, and the residue was extracted with pentane and filtered through celite. The pentane was then reduced to a minimal volume under reduced pressure and the solvent was allowed to concentrate slowly overnight by slow evaporation into an HMDSO antisolvent at room temperature. The mother liquor was decanted and the solids were washed with HMDSO (3 x 1 mL). This yielded red-brown crystalline material of **{TPBFeNO}^{9}** (yield = 21.3 mg, 68%).
^{1}H NMR (C_6D_6, 400 MHz, RT): 17.48 (3 H), 11.27 (3 H), 8.58 (3 H), 6.11 (3 H), 2.11 (9H), 1.87 (9H), 0.57 (3 H), -1.23 (9H), -2.10 (9 H).
μ_{eff} (RT, Evans Method, C_6D_6): 1.7μ_B.
IR (Thin Film): 1664 cm^{-1} (ν_{NO}).
UV/Vis (2-MeTHF, nm {cm^{-1} M^{-1}}): 535 {420}, 916 {180}.
Elemental Analysis: theory [C 63.93, H 8.05, N 2.07]; found [63.59, 8.11, 2.18]

{TPBFeNO}^{10}-[TPBFeNO][PF_6] (66.3 mg, 0.081 mmol, 1.0 eq.) was suspended in THF (10 mL) and added to a vial containing 1% Na/Hg amalgam (3.8 mg of Na, 0.162 mmol, 2.0 eq.). The suspension was stirred at room temperature for four hours yielding a dark red solution. The solvent was removed under reduced pressure, and the residue was extracted with ether (3 x 3 mL) and filtered through celite. The solvent was then evaporated to dryness under reduced pressure. The residue was dissolved in minimal THF (~2 mL) and layered with a 2 mL benzene solution of 12-crown-4 (47 mg, 0.267 mmol, 3.3 eq.). After standing at room temperature overnight, red needles of the desired compound were obtained. Decanting and washing with minimal ether and then drying yielded **{TPBFeNO}^{10}** (48 mg, 57 %). The best yields could be

obtained using this procedure but reduction of **{TPBFeNO}^{9}** with 1 eq. of Na/Hg and the above reported isolation procedure also led reproducibly to pure material.
^{1}H NMR (-78 °C, THF-d_8, 500 MHz): δ = 7.15 (3 H, br s, Ar-*H*), 7.01 (3 H, br s, Ar-*H*), 6.73 (3 H, br s, Ar-*H*), 6.59 (3 H, br s, Ar-*H*), 3.74 (32 H, s, 12-c-4), 2.79 (3 H, br s, PC*H*), 2.00 (3 H, br s, PC*H*), 1.52-0.80 (27 H, m, PCHCH_3), -0.43 (9H, s, PCHCH_3).
^{31}P NMR (-78 °C, THF-d_8, 202 MHz): δ = 88.7 (br).
^{11}B NMR (RT, THF-d_8, 128 MHz): δ = 19.9 (br).
^{13}C NMR (-78 °C, 126 MHz, THF-d_8, 100 MHz): δ = 175.9 (br), 146.0, 130.7, 125.2, 124.9, 119.9, 70.4, 65.1, 30.7, 27.6, 20.3, 18.9, 17.2.
At room temperature there is no detectable ^{31}P NMR signal and the ^{1}H NMR spectrum is broadened presumably by the presence of undetectably small amounts of **{TPBFeNO}^{9}** that undergoes fast electron transfer with **{TPBFeNO}^{10}** in solution. Cooling the solution to -78 °C makes this process slower than the NMR time scale allowing ^{1}H and ^{31}P NMR spectra to be obtained.
IR (Thin Film): 1568 cm^{-1} (ν_{NO}).
UV/Vis (2-MeTHF, nm {cm^{-1} M^{-1}}): 314 {11700}, 389 {4000}, 499 {1800}.
Elemental Analysis: **{TPBFeNO}^{10}·.5C_6H_6** theory [C 60.56, H 8.22, N 1.28]; found [C 60.32, H 8.10, N 1.41]
Taking crystalline **{TPBFeNO}^{10}** and then pulling vacuum on it before dissolution in THF-d_8 leads to the presence of 0.5 equivalents of C_6H_6 as seen in **Figure S9**. The crystal structure of **{TPBFeNO}^{10}** has two half-occupied benzene molecules present confirming the presence of benzene in crystalline **{TPBFeNO}^{10}**.

NMR Spectra:

Figure S1: The ^{1}H NMR spectrum (500 MHz) of **{TPBFeNO}^{8}** at room temperature in THF-d_8.

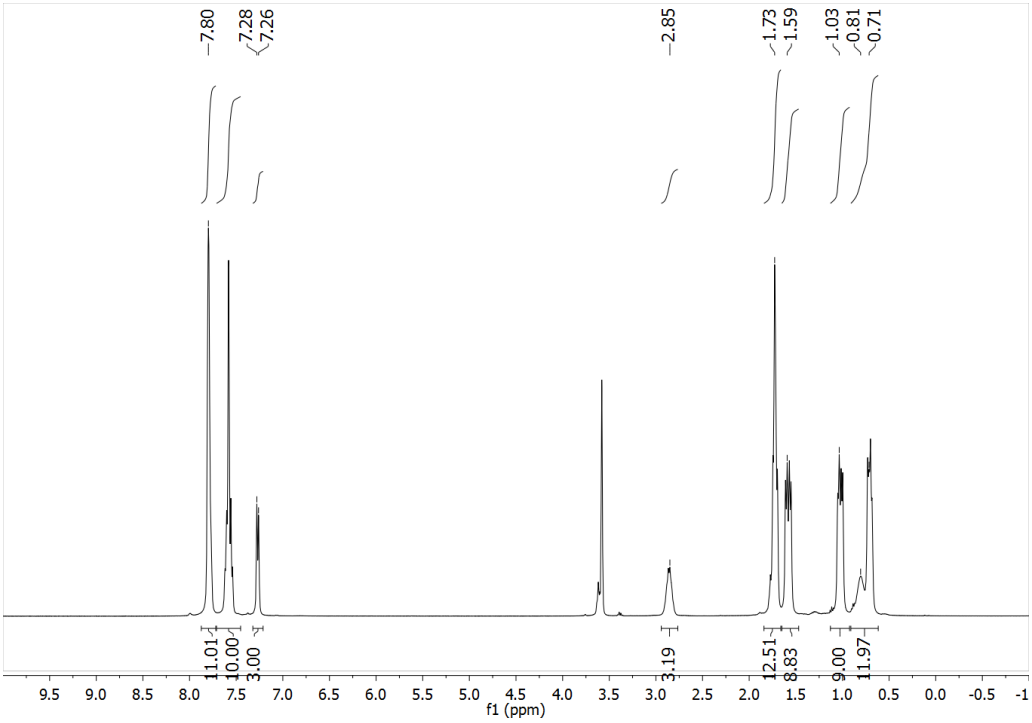


Figure S2: The ^{1}H NMR spectrum (500 MHz) of **{TPBFeNO}^{8}** at -78 °C in THF-d_8.

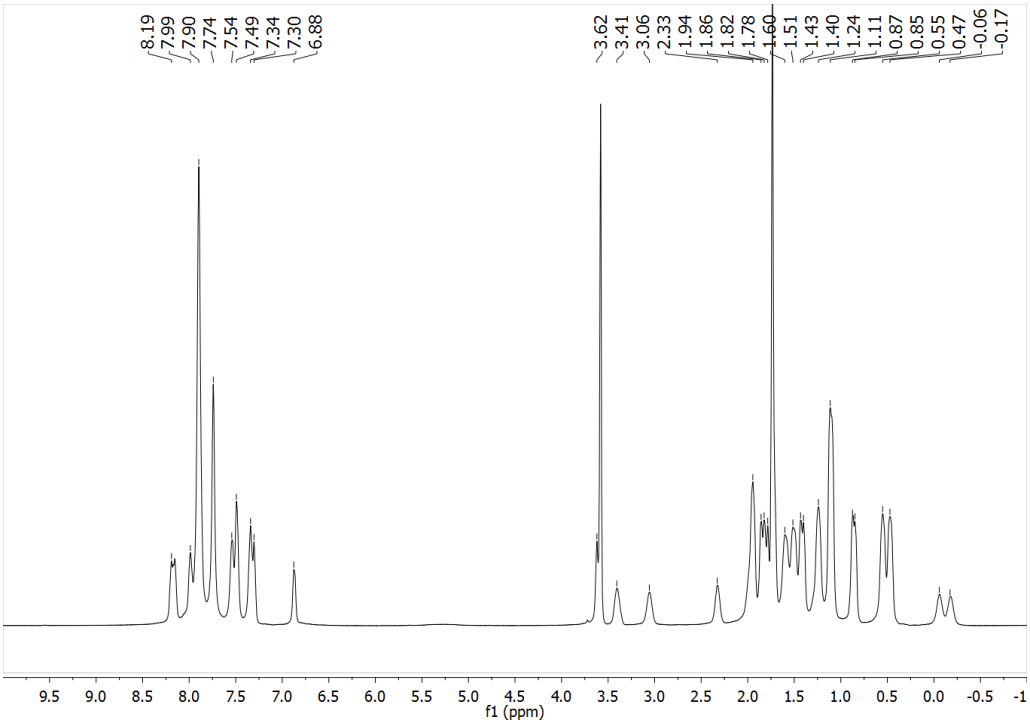


Figure S3: The ^{31}P NMR spectrum (161.9 MHz) of **{TPBFeNO}^{8}** at room temperature in THF-d_8.

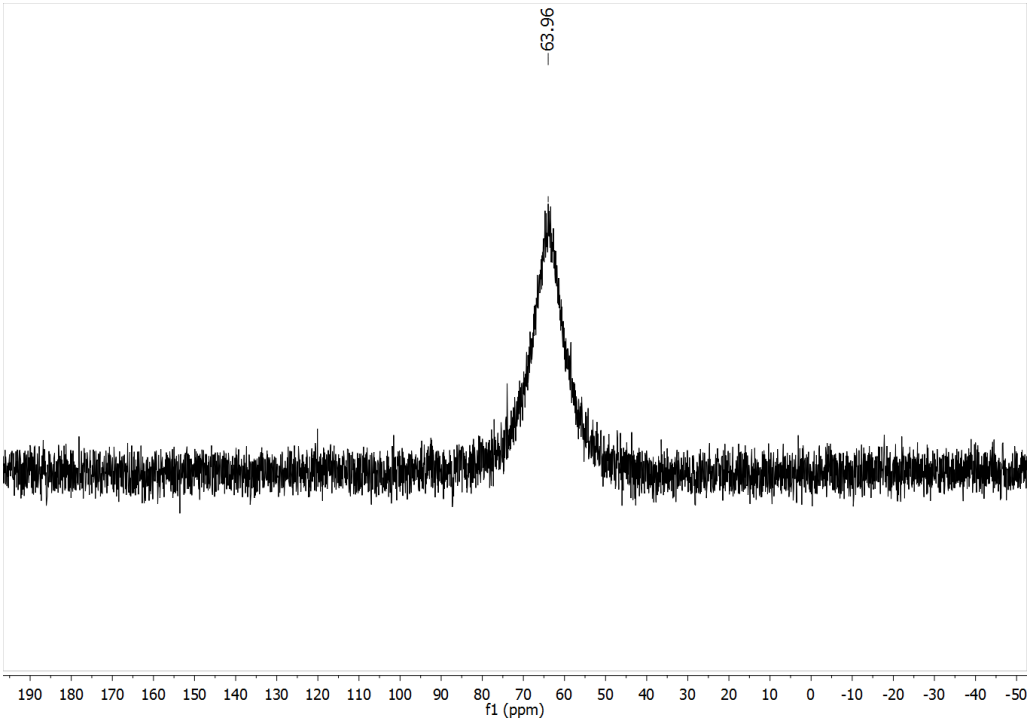


Figure S4: The ^{31}P NMR spectrum (202.4 MHz) of **{TPBFeNO}^{8}** at -78 °C in THF-d_8.

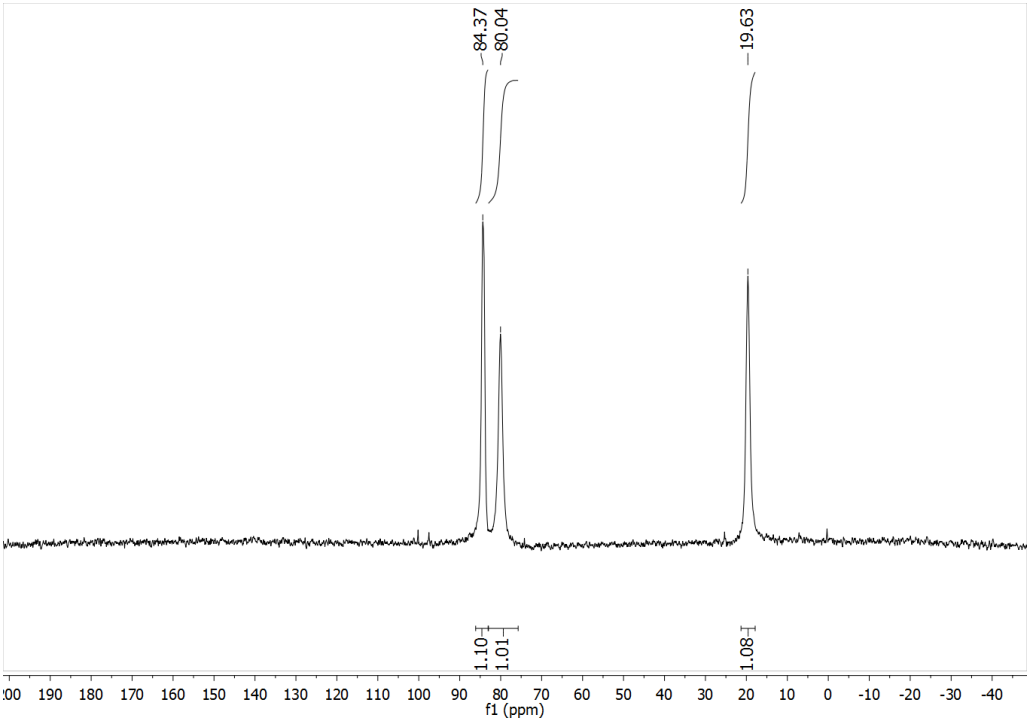


Figure S5: The ^{11}B NMR spectrum (128.3 MHz) of **{TPBFeNO}^{8}** at room temperature in THF-*d*$_8$.

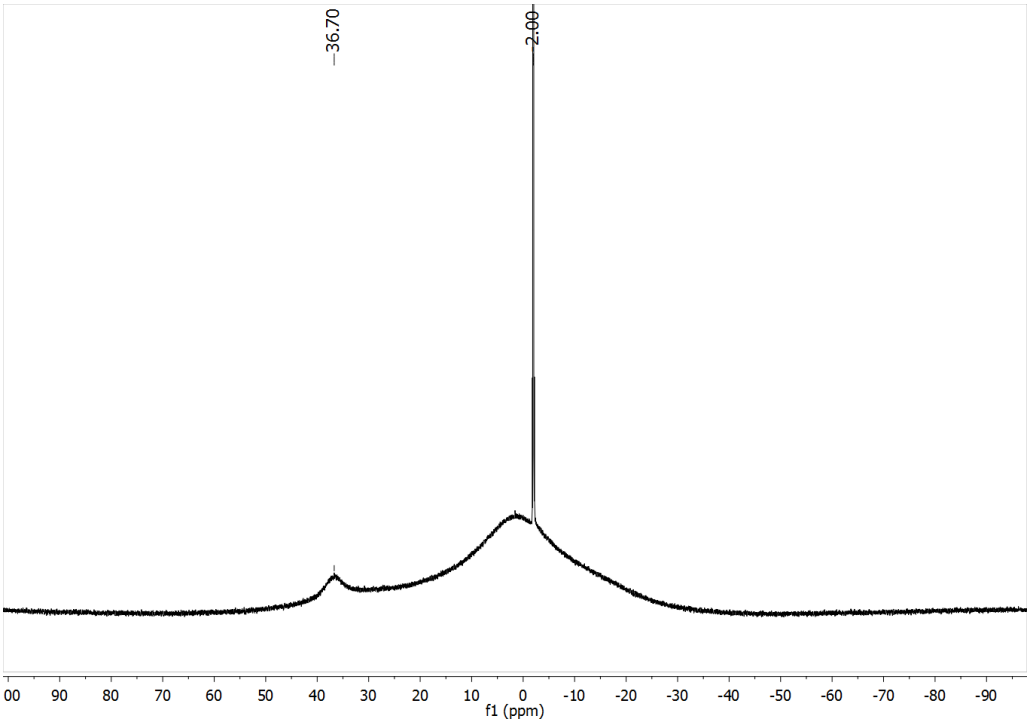


Figure S6: The ^{19}F NMR spectrum (376.3 MHz) of **{TPBFeNO}^{8}** at room temperature in THF-*d*$_8$.

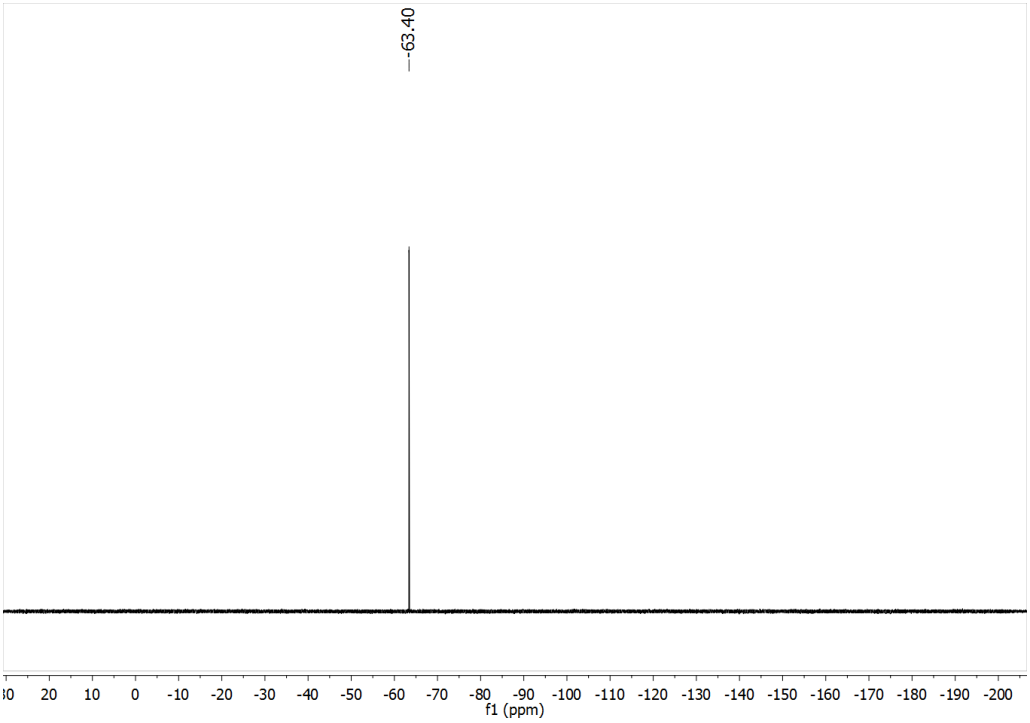


Figure S7: The ^{13}C NMR spectrum (100.6 MHz) of **{TPBFeNO}^{8}** at room temperature in THF-d_8.

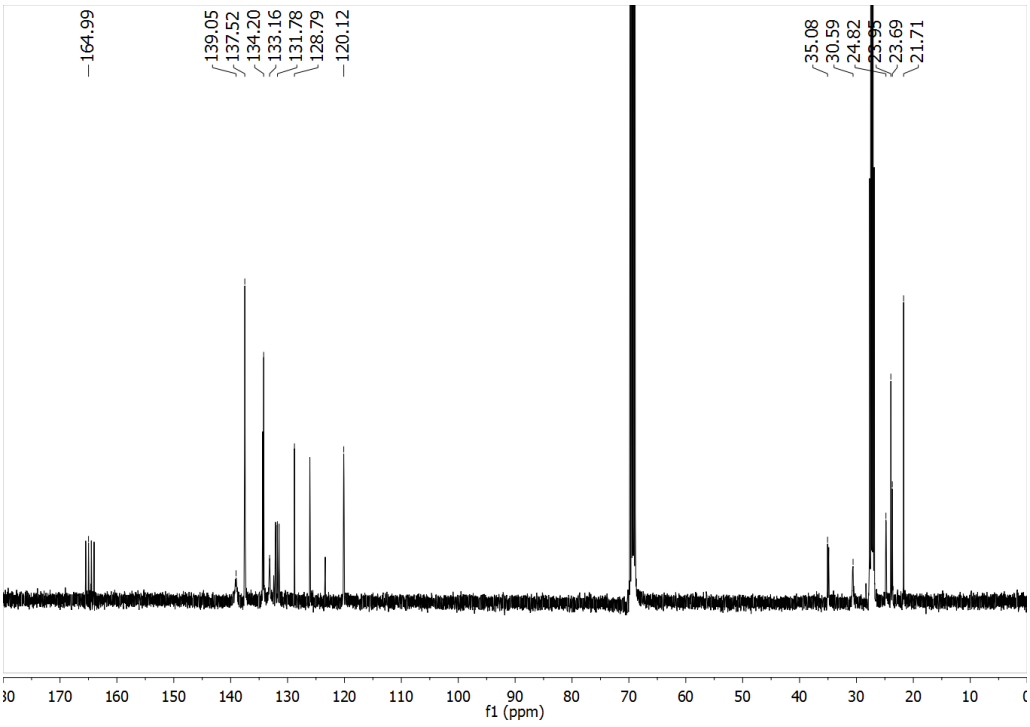


Figure S8: The ^{1}H NMR spectrum (400 MHz) of **{TPBFeNO}^{9}** at room temperature in C_6D_6.

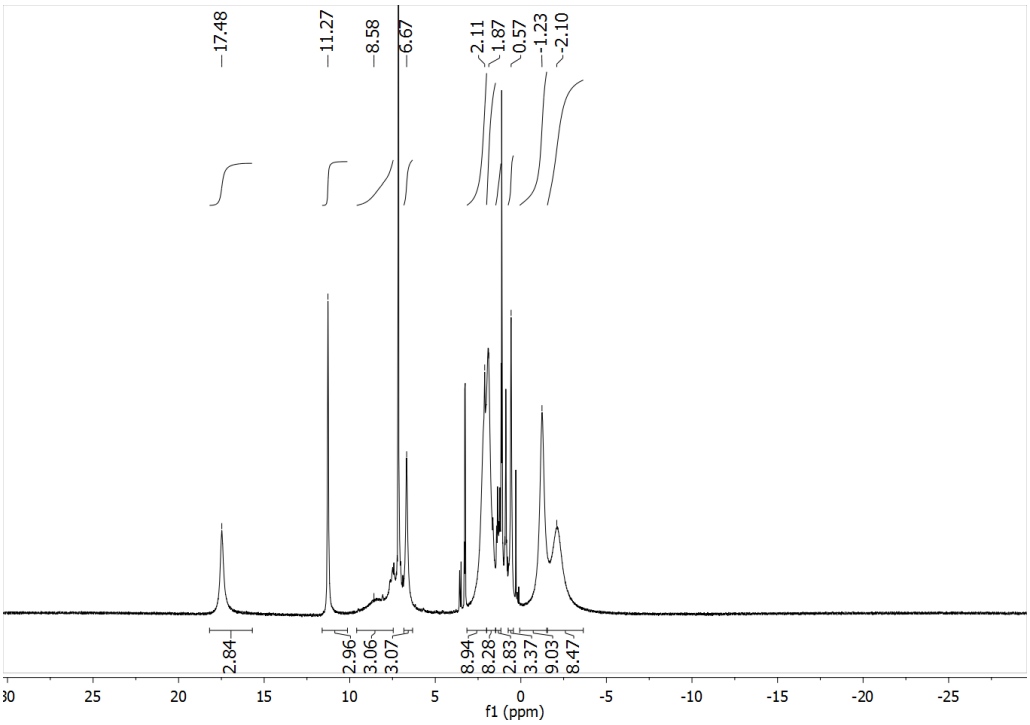


Figure S9: The ^{1}H NMR spectrum (500 MHz) of **{TPBFeNO}^{10}** at room temperature in THF-d_8.

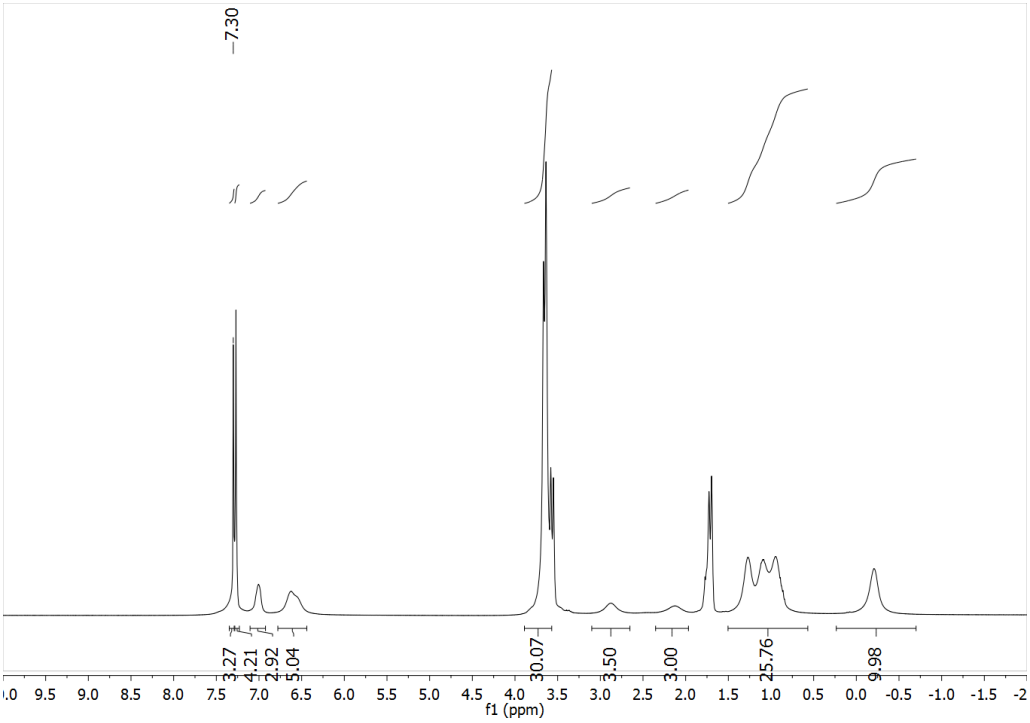


Figure S10: The ^{1}H NMR spectrum (500 MHz) of **{TPBFeNO}^{10}** at -78 °C in THF-d_8.

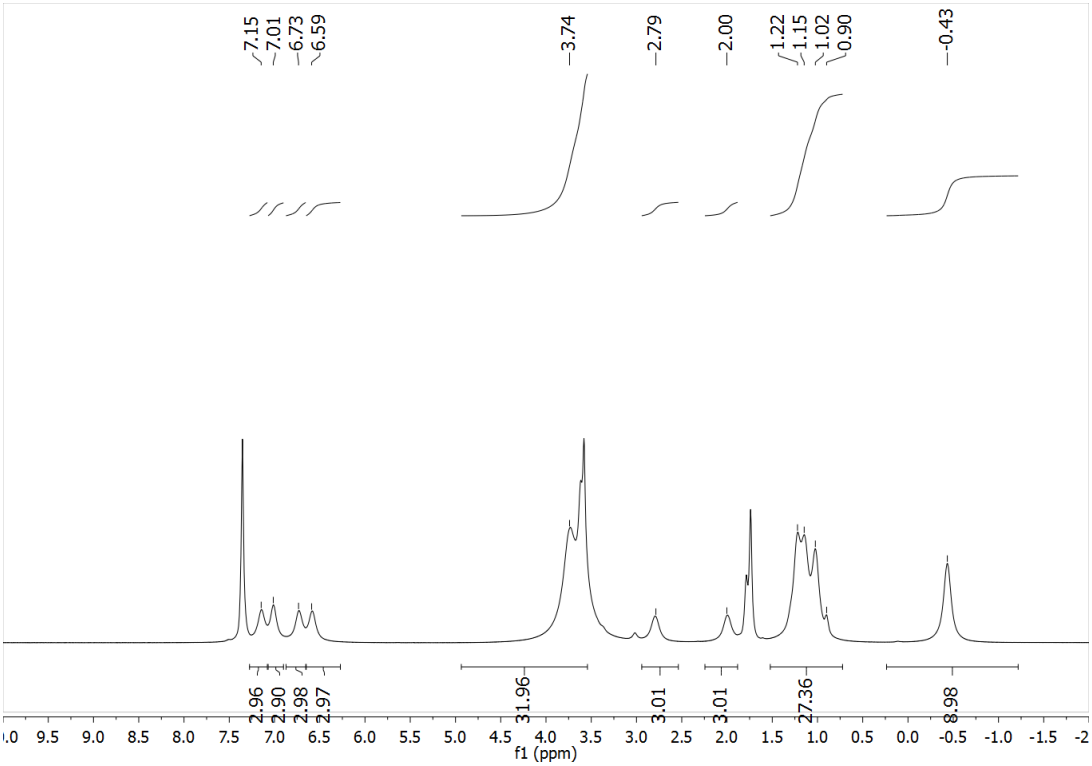


Figure S11: The ^{31}P NMR spectrum (202.4 MHz) of **{TPBFeNO}^{10}** at -78 °C in THF-d_8.

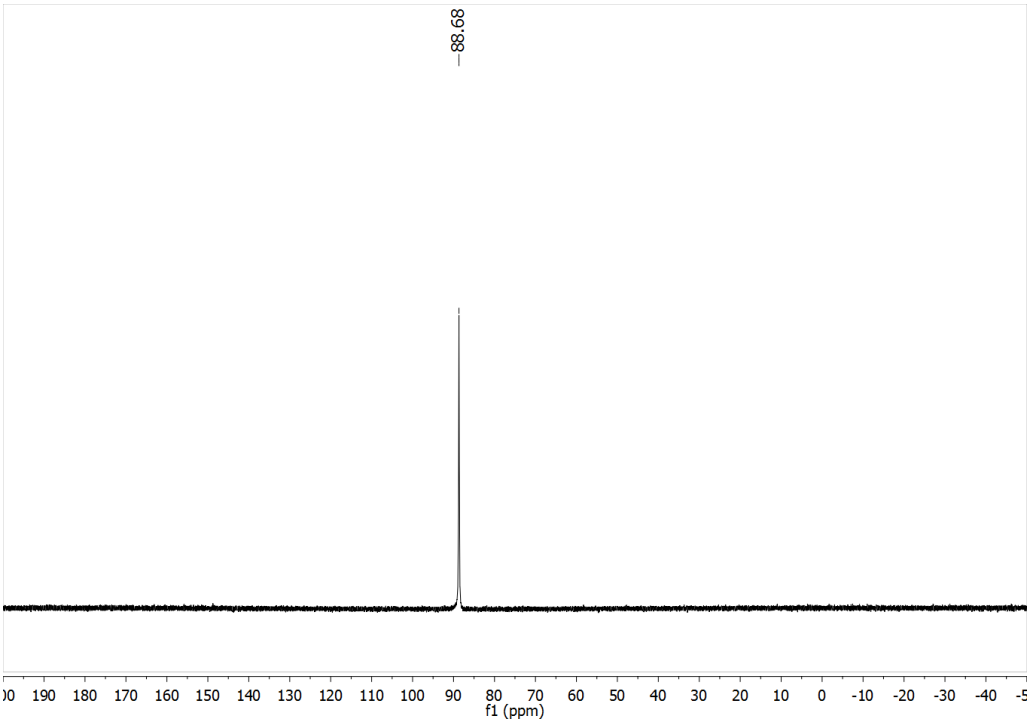


Figure S12: The ^{11}B NMR spectrum (128.3 MHz) of **{TPBFeNO}^{10}** at room temperature in THF-d_8.

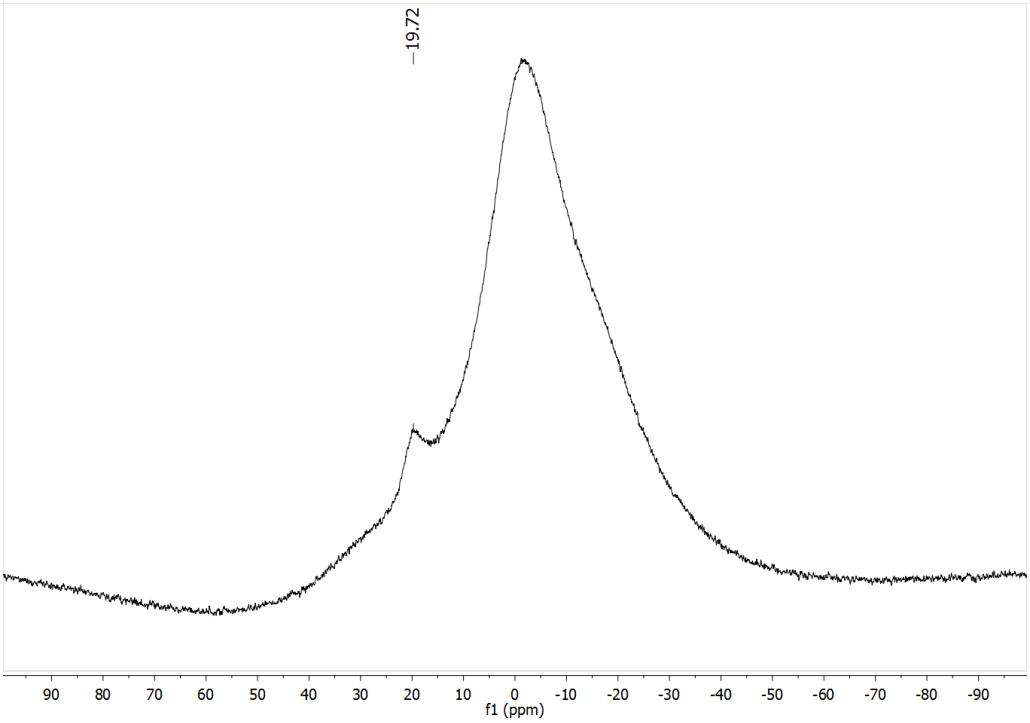
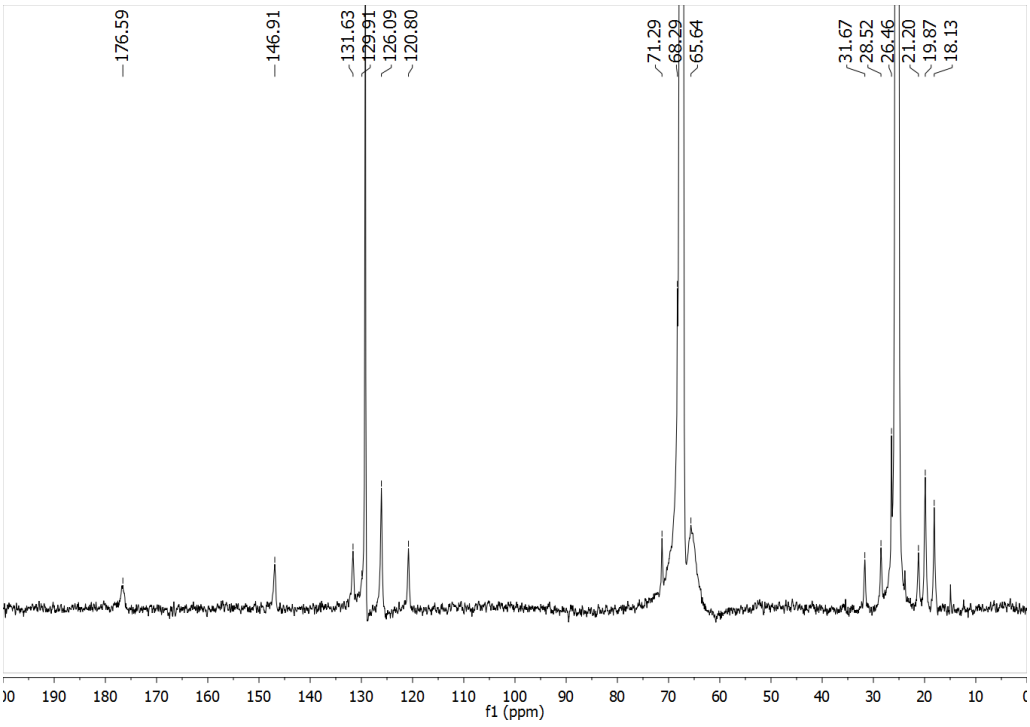


Figure S13: The ^{13}C NMR spectrum (125.7 MHz) of **{TPBFeNO}^{10}** at -78 °C in THF-d_8.



IR Spectra:

Figure S14: Thin-film IR Absorption spectrum of **{TPBFeNO}^{8}**.

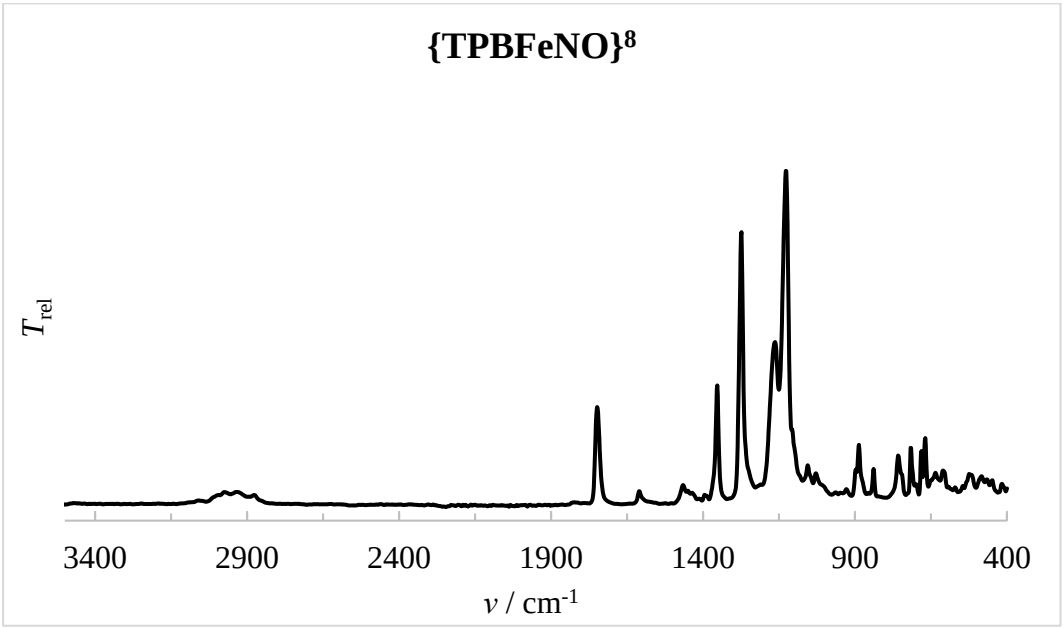


Figure S15: Thin-film IR Absorption spectrum of **{TPBFeNO}^{9}**.

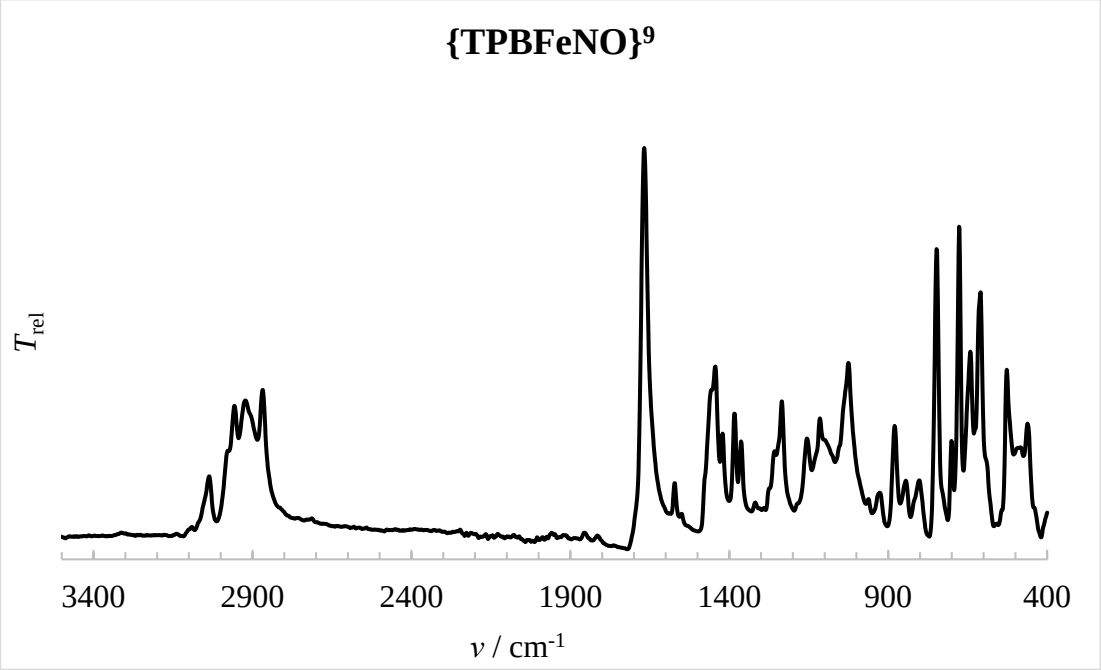
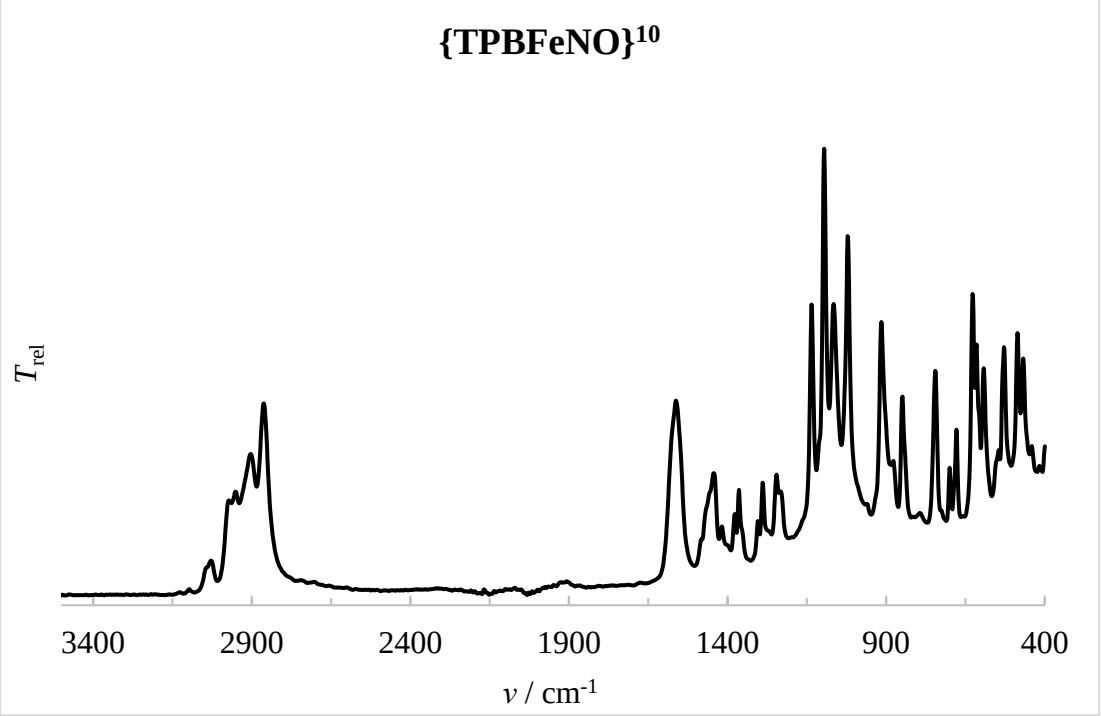


Figure S16: Thin-film IR Absorption spectrum of **{TPBFeNO}^{10}**.



UV/Visible Spectra:

Figure S17: UV/Visible spectra of **{TPBFeNO}^{8}** in 2-MeTHF accounting for changes in density with temperature.[5]

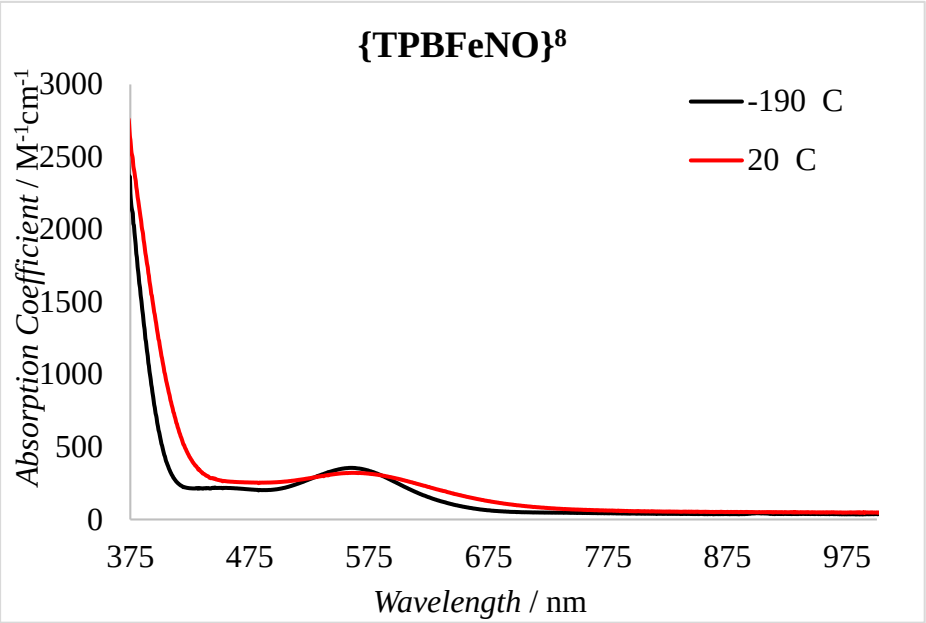


Figure S18: UV/Visible spectra of **{TPBFeNO}^{10}** in 2-MeTHF accounting for changes in density with temperature.[5]

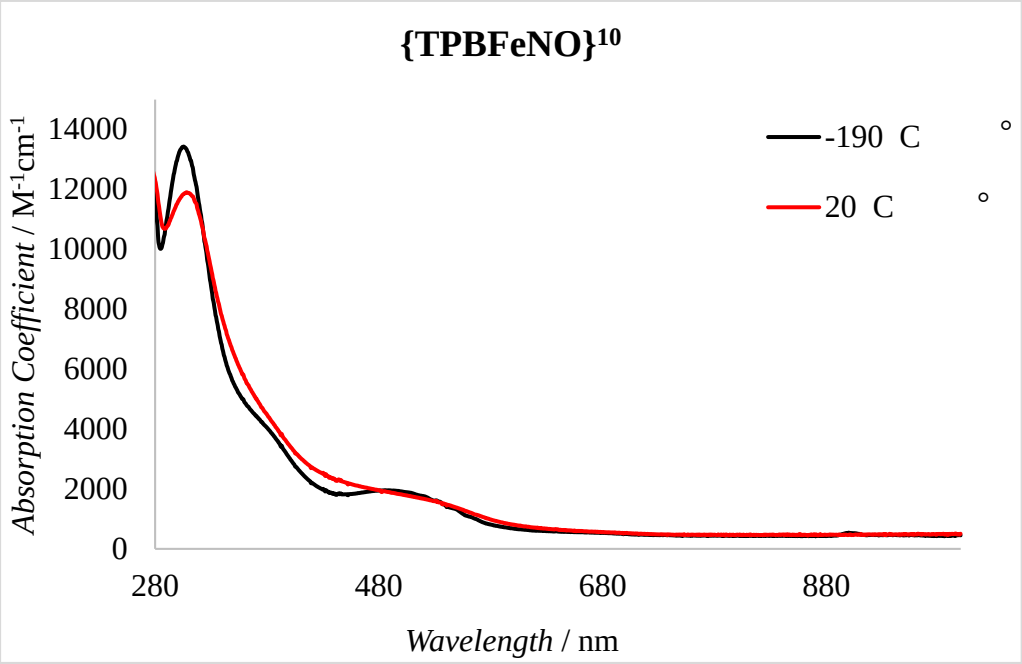


Table S1: Comparison of selected data for **{TPBFeNO}^{9}** and $[Cr(CN)_5(NO)]^{3-}$.[17]

Property	{TPBFeNO}^{9}	$[Cr(CN)_5(NO)]^{3-}$
ν(NO) (cm^{-1})	1667	1645
d(N-O) (Å)	1.1901(7)	1.207(12)
∡(M-N-O) (°)	176.18(6)	175.6(1)
ε_{max} (nm)	521	450

^{57}Fe Mössbauer Spectra:

Mössbauer Discussion: There are a variety of mechanisms that can lead to an asymmetric quadrupole doublet arising. The most common cause is the presence of a local magnetic field (usually from the measured iron complex being paramagnetic) that causes a difference in the relaxation rate of the nuclear transitions.[18] However, other mechanisms can cause broad and asymmetric line shapes even in diamagnetic samples particularly when they are measured as crystalline or microcrystalline solids. Such phenomena include the Goldanskii-Kargaryin effect,[19] "texture,"[20] or cosine smearing.[21] Despite the appearance of asymmetric line shapes in the crystalline, 80 K, zero field Mössbauer of **{TPBFeNO}^{8}** and **{TPBFeNO}^{10}** we believe that these species are diamagnetic in the solid state. The X-ray structures manifest short metal-ligand bond lengths that are well predicted by DFT calculations with an $S = 0$ ground state. In contrast optimizations from using the crystal structures as input in an $S = 1$ or 2 ground state lead to considerably different structures and higher energies. To further verify that the bulk material was diamagnetic we performed 80 K, zero field Mössbauer on powdered samples obtained by dissolving crystalline material in THF, evaporating the solvent and then triturating it with pentane. This procedure led to the obtainment of signals with symmetric line shapes and in the case of **{TPBFeNO}^{10}** significantly sharper line widths.

Furthermore the spin state of **{TPBFeNO}^{8}** and **{TPBFeNO}^{10}** is known to be $S = 0$ in solution due to the multinuclear NMR data. As such 2 mM THF solutions of ^{57}Fe enriched samples of **{TPBFeNO}^{8}** and **{TPBFeNO}^{10}** were measured in the presence (50 mT) and absence of a magnetic field. These samples also manifested the same isomer shift and quadrupole splitting as the solid samples confirming that the spin state is the same in solution and solid state. In the **{TPB^{57}FeNO}^{10}** there is the presence of a ~20 % contamination of **[TPBFeN$_2$]$^-$**. This contaminant was verified by the measurement of an independently prepared sample of **[TPBFeN$_2$]$^-$**. As can be seen in the electrochemistry under N_2 (**Figure S32**), addition of excess strong reductant leads to the formation of **[TPBFeN$_2$]$^-$** from samples of **{TPBFeNO}^{8}**. Such an issue can be readily avoided on large scale syntheses of **{TPBFeNO}^{10}** by the use of stoichiometric reducing agent but in the preparation of small amounts of ^{57}Fe enriched material (~ 2 mg) consistent over reduction was observed. However the presence of this impurity does not

prevent the observation of symmetric and narrow linewidths for solution state measurements of **{TPBFeNO}^{10}**.

The calculated Mössbauer parameters (**Table S5**) consistently underestimate the isomer shift by ~ 0.08 mm s^{-1} an error within the standard found by Neese and coworkers.[16] The predictions of the quadrupole splitting are remarkably accurate within 0.04 mm s^{-1} in all cases. These calculations also illustrate the trend discussed in the main text in which lower spin states are associated with low isomer shifts.

Figure S19: The 80 K, zero field ^{57}Fe Mössbauer of **{TPBFeNO}^{8}** as a microcrystalline solid suspended in a boron nitride matrix. Fit with δ = 0.24 mm s^{-1}, Δ_{Eq} = 1.50 mm s^{-1}, Γ_R = 0.34 mm s^{-1}, and Γ_L = 0.29 mm s^{-1}.

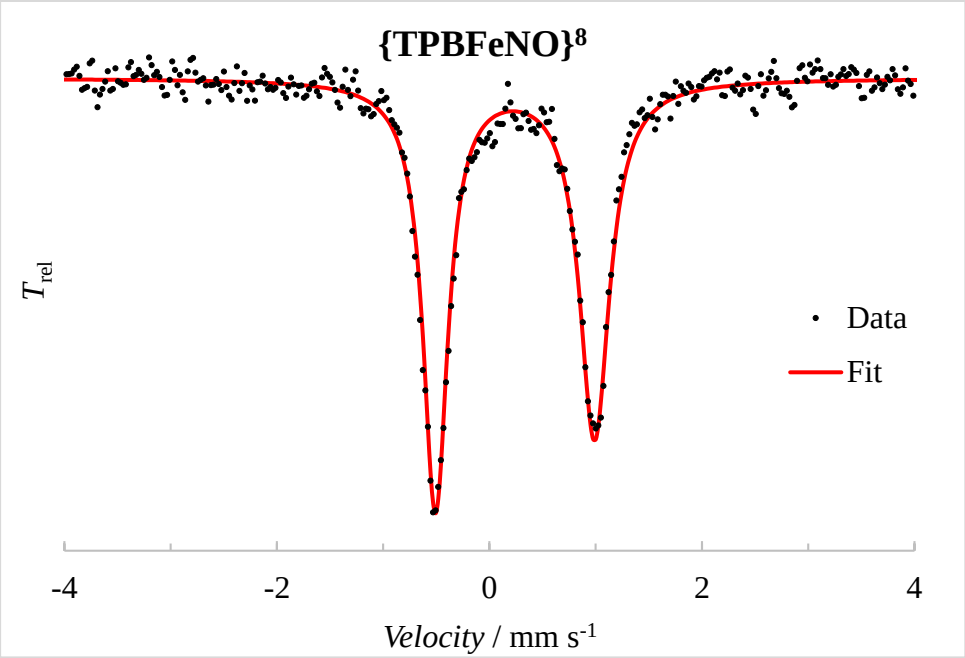


Figure S20: The 80 K, zero field ^{57}Fe Mössbauer of **{TPBFeNO}^{8}** as a powder suspended in a boron nitride matrix. Fit with δ = 0.24 mms^{-1}, Δ_{Eq} = 1.50 mm s^{-1}, Γ_R = 0.34 mm s^{-1}, and Γ_L = 0.34 mm s^{-1}.

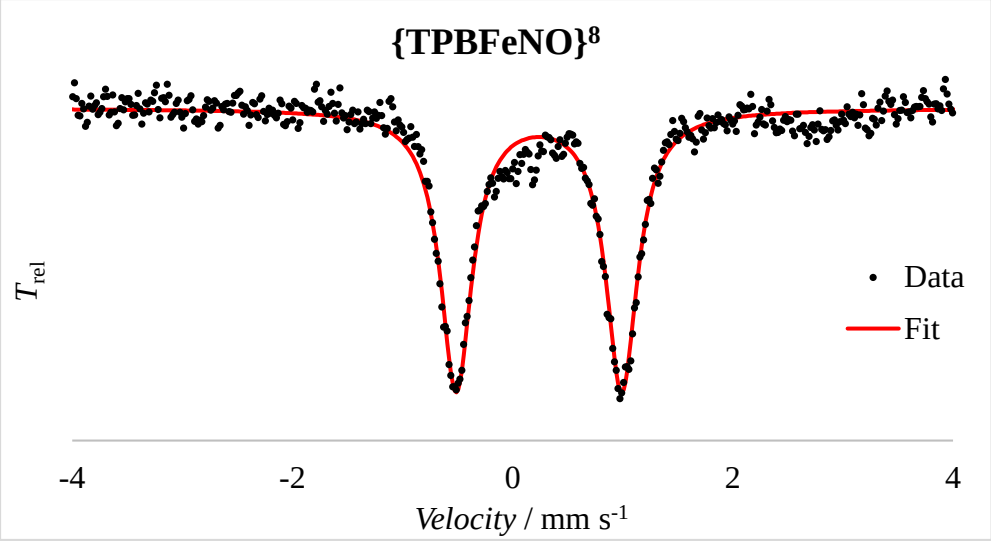


Figure S21: The 80 K, zero field ^{57}Fe Mössbauer of a 2mM solution of **{TPB^{57}FeNO}^{8}** in 2-MeTHF. Fit with δ = 0.25 mm s^{-1}, Δ_{Eq} = 1.47 mm s^{-1}, Γ_R = 0.27 mm s^{-1}, and Γ_L = 0.27 mm s^{-1}.

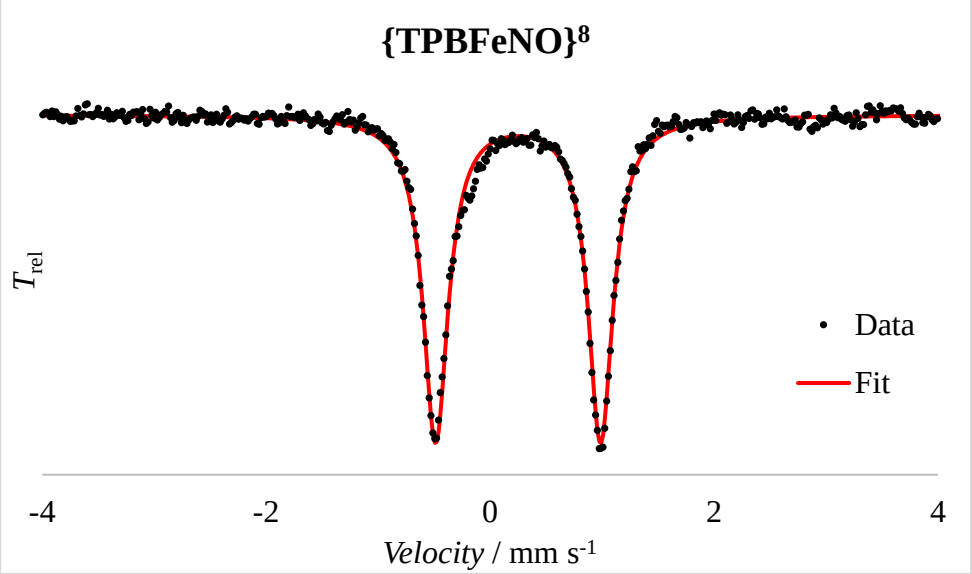


Figure S22: The 80 K, 50 mT ^{57}Fe Mössbauer of a 2mM solution of **{TPB^{57}FeNO}^{8}** in 2-MeTHF. Fit with δ = 0.25 mm s^{-1}, Δ_{Eq} = 1.46 mm s^{-1}, Γ_R = 0.28 mm s^{-1}, and Γ_L = 0.28 mm s^{-1}.

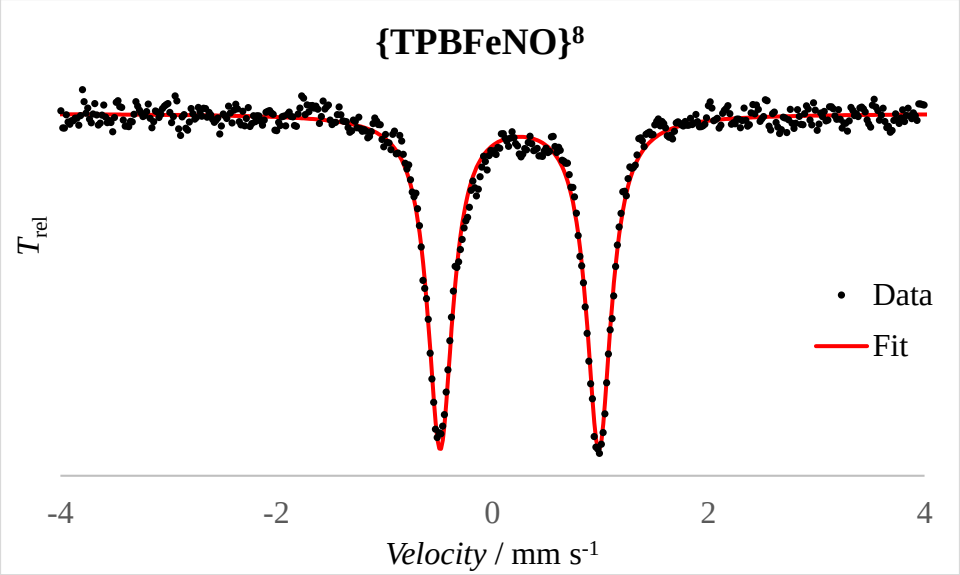


Figure S23: The 80 K, zero field ^{57}Fe Mössbauer of **{TPBFeNO}^{9}** as a microcrystalline solid suspended in a boron nitride matrix. Fit with δ = 0.26 mm s^{-1}, Δ_{Eq} = 0.92 mm s^{-1}, Γ_R = 0.34 mm s^{-1}, and Γ_L = 0.31 mm s^{-1}.

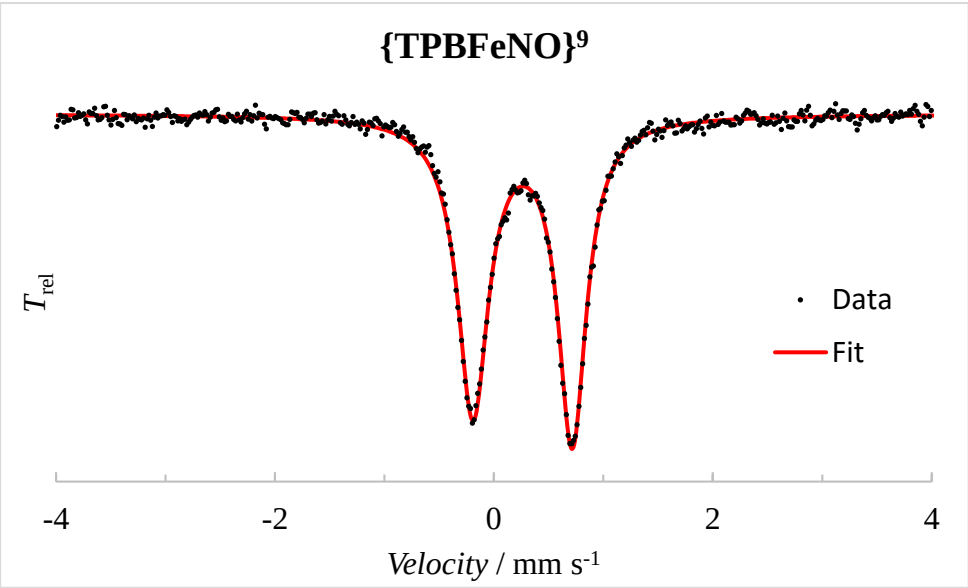


Figure S24: The 80 K, zero field ^{57}Fe Mössbauer of **{TPBFeNO}^{10}** as a microcrystalline solid suspende in a boron nitride matrix. Fit with δ = 0.17 mm s^{-1}, Δ_{Eq} = 1.62 mm s^{-1}, Γ_R = -0.61 mm s^{-1}, and Γ_L = -0.64 mm s^{-1}. Given the microcrystalline nature of the material a Voigtian distribution was considered to be an appropriate model,[13,17] and the purity of the material was confirmed by NMR and IR spectroscopy. The most likely impurity would be **{TPBFeNO}^{9}** due to the handling procedure needed to mount the Mössbauer sample, but including a second species with the parameters for **{TPBFeNO}^{9}** leads to that component only representing 1% of the total intensity and no improvement of the fit as judged by the χ^2-value.

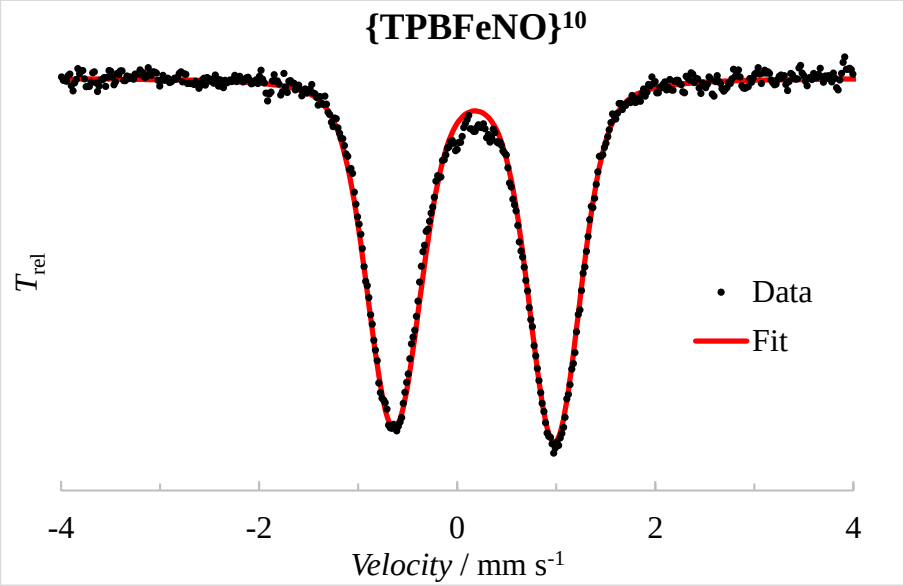


Figure S25: The 80 K, zero field ^{57}Fe Mössbauer of **{TPBFeNO}^{10}** as a powder suspended in a boron nitride matrix. Fit with δ = 0.16 mm s^{-1}, Δ_{Eq} = 1.62 mm s^{-1}, Γ_R = 0.44 mm s^{-1}, and Γ_L = 0.44 mm s^{-1}.

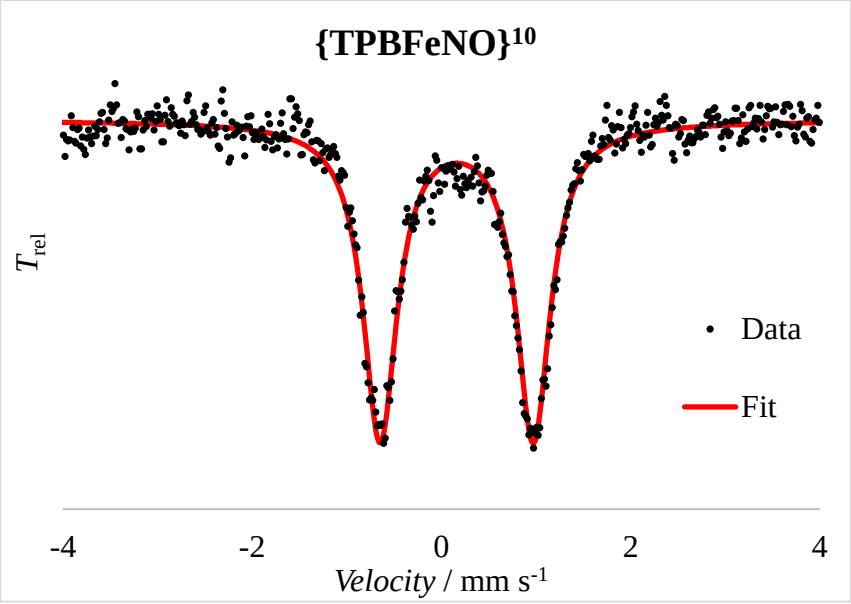


Figure S26: The 80 K, zero field ^{57}Fe Mössbauer of a 2 mM solution of **{TPB^{57}FeNO}^{10}** in THF. Fit for **{TPBFeNO}^{10}** δ = 0.17 mm s^{-1}, Δ_{Eq} = 1.64 mm s^{-1}, Γ_R = 0.26 mm s^{-1}, and Γ_L = 0.26 mm s^{-1} Weight = 0.81. Fit for **[TPBFeN$_2$]$^-$** δ = 0.36 mm s^{-1}, Δ_{Eq} = 0.95 mm s^{-1}, Γ_R = 0.67 mm s^{-1}, and Γ_L = 0.67 mm s^{-1} Weight = 0.19.

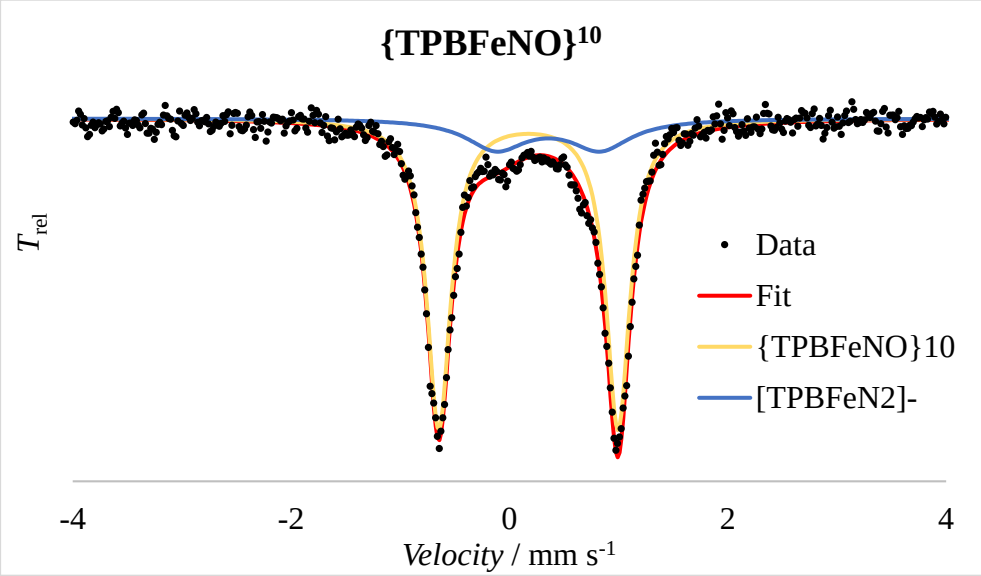


Figure S27: The 80 K, 50 mT parallel field ^{57}Fe Mössbauer of a 2mM solution of **{TPB^{57}FeNO}^{10}** in THF. Fit for **{TPBFeNO}^{10}** δ = 0.17 mm s^{-1}, Δ_{Eq} = 1.64 mm s^{-1}, Γ_R = 0.36 mm s^{-1}, and Γ_L = 0.36 mm s^{-1} Weight = 0.81. Fit for **[TPBFeN$_2$]$^-$** δ = 0.36 mm s^{-1}, Δ_{Eq} = 0.95 mm s^{-1}, Γ_R = 0.54 mm s^{-1}, and Γ_L = 0.54 mm s^{-1} Weight = 0.19.

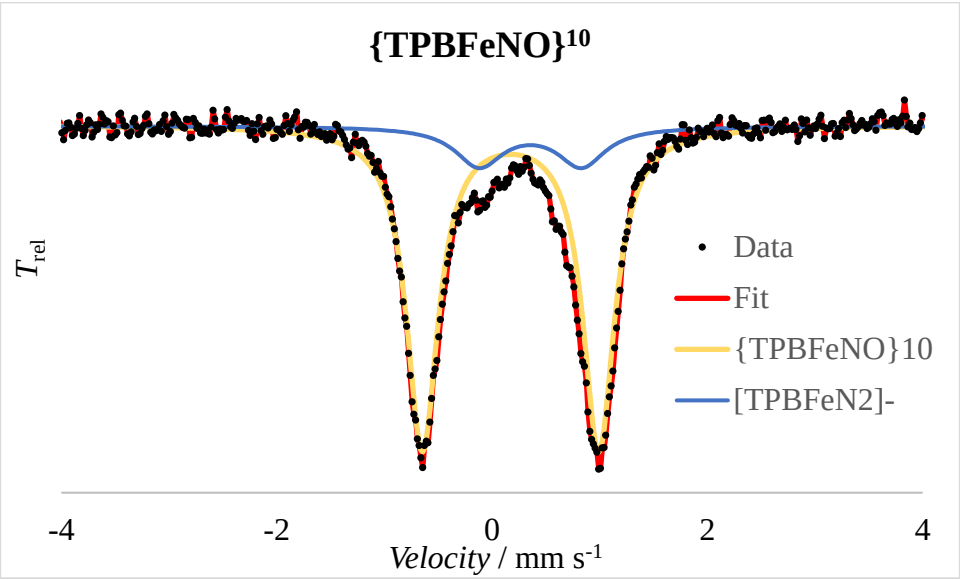


Figure S28: The 80 K, 50 mT perpendicular field ^{57}Fe Mössbauer of a 2mM solution of **{TPB^{57}FeNO}^{10}** in THF. Fit for **{TPBFeNO}^{10}** δ = 0.17 mm s^{-1}, Δ_{Eq} = 1.63 mm s^{-1}, Γ_R = 0.26 mm s^{-1}, and Γ_L = 0.26 mm s^{-1} Weight = 0.78. Fit for **[TPBFeN$_2$]$^-$** δ = 0.36 mm s^{-1}, Δ_{Eq} = 0.95 mm s^{-1}, Γ_R = 0.54 mm s^{-1}, and Γ_L = 0.54 mm s^{-1} Weight = 0.22.

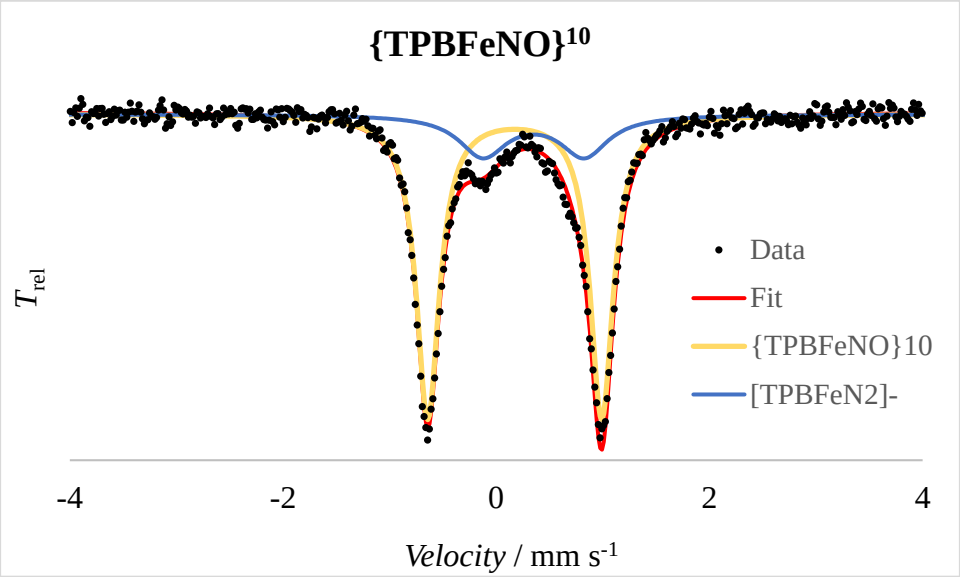
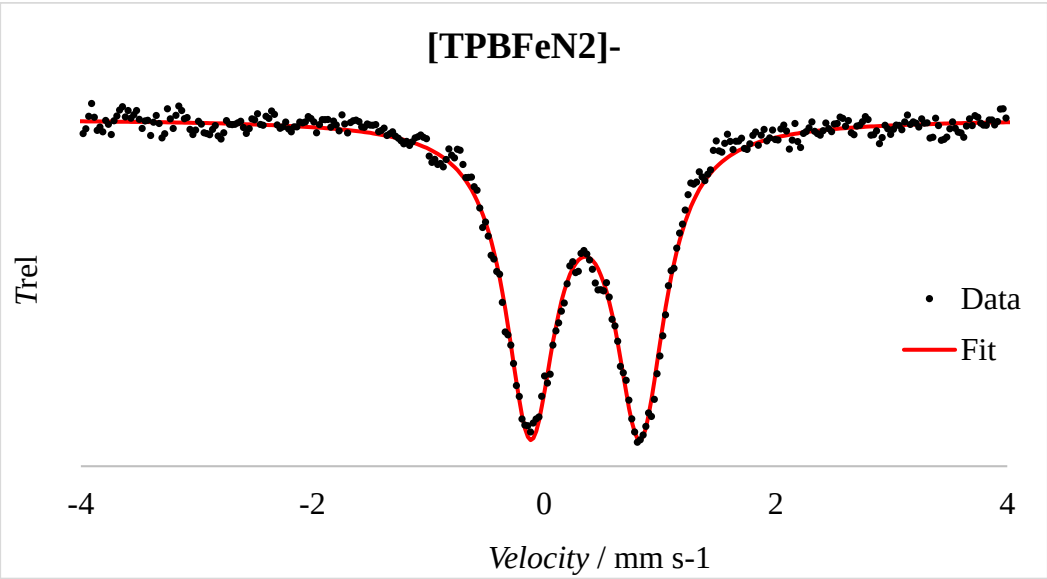


Figure S29: The 80 K, 50 mT parallel field Mössbauer of **[TPBFeN$_2$]$^-$** ([TPBFeN$_2$][Na(12-crown-4)$_2$]) as a powder suspended in a boron-nitride matrix. Fit with δ = 0.36 mm s^{-1}, Δ_{Eq} = 0.95 mm s^{-1}, Γ_R = 0.52 mm s^{-1}, and Γ_L = 0.52 mm s^{-1}.



Electrochemistry:

Figure S30: Cyclic voltammetry data at 100 mV s^{-1} for **{TPBFeNO}^{8}** in a THF solution of 0.1 M [TBA][PF_6] under argon.

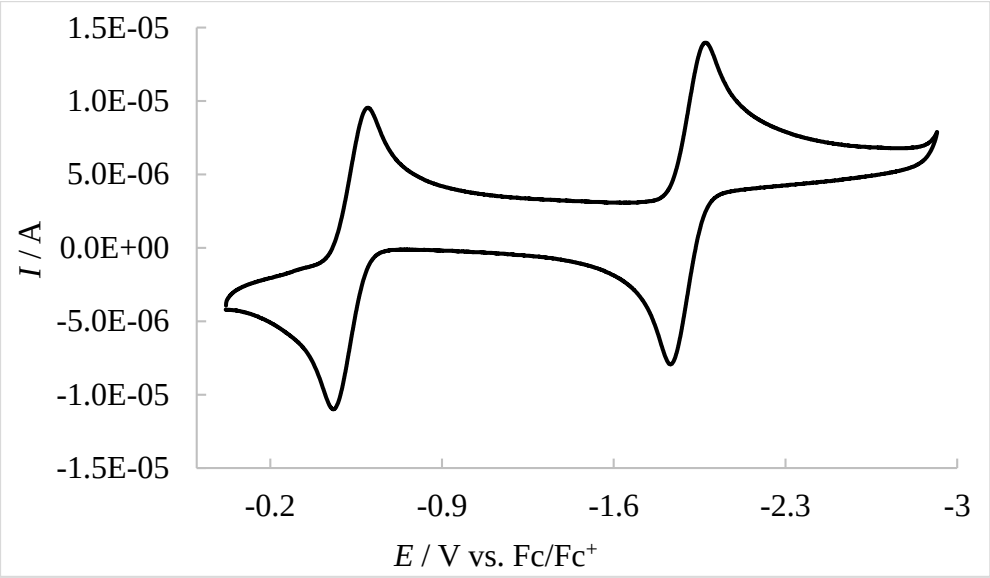


Figure S31: Scan rate dependence of the **{TPBFeNO}$^{8/9}$** couple in a THF solution of 0.1 M [TBA][PF_6] under argon.

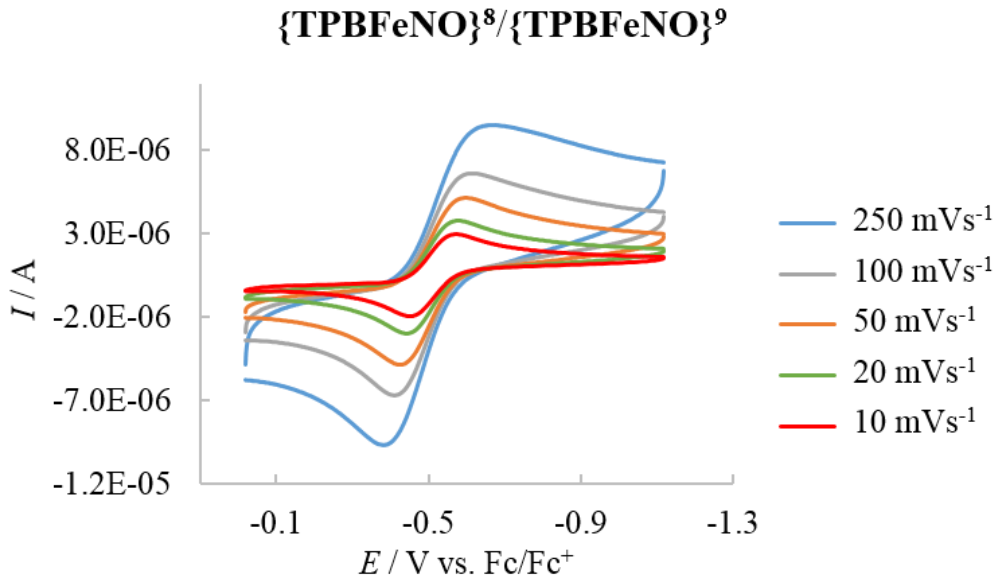


Figure S32: Scan rate dependence of the **{TPBFeNO}$^{9/10}$** couple in a THF solution of 0.1 M [TBA][PF_6] under argon.

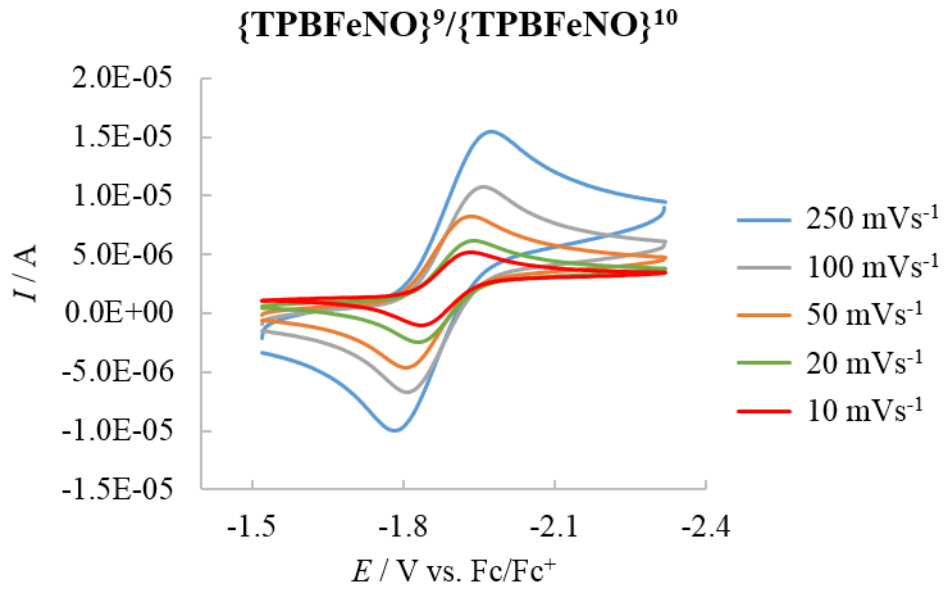
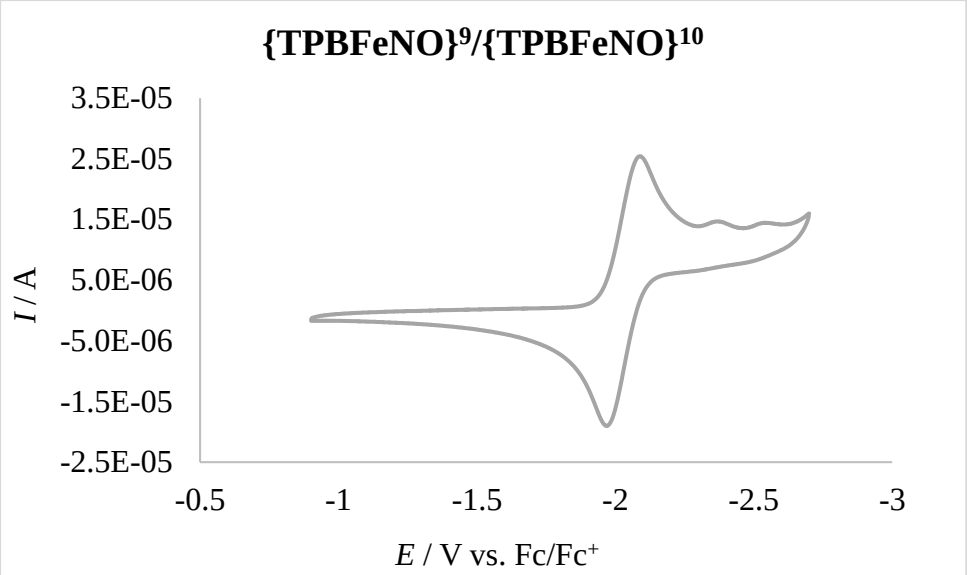


Figure S33: Cyclic voltammetry data at 100 mV s^{-1} for **{TPBFeNO}^{8}** in a THF solution of 0.1 M [TBA][BArF] under N_2.



X-ray Crystallography Data:

Table S2: X-ray parameters for **{TPBFeNO}^{8}**, **{TPBFeNO}^{9}**, and **{TPBFeNO}^{10}**.

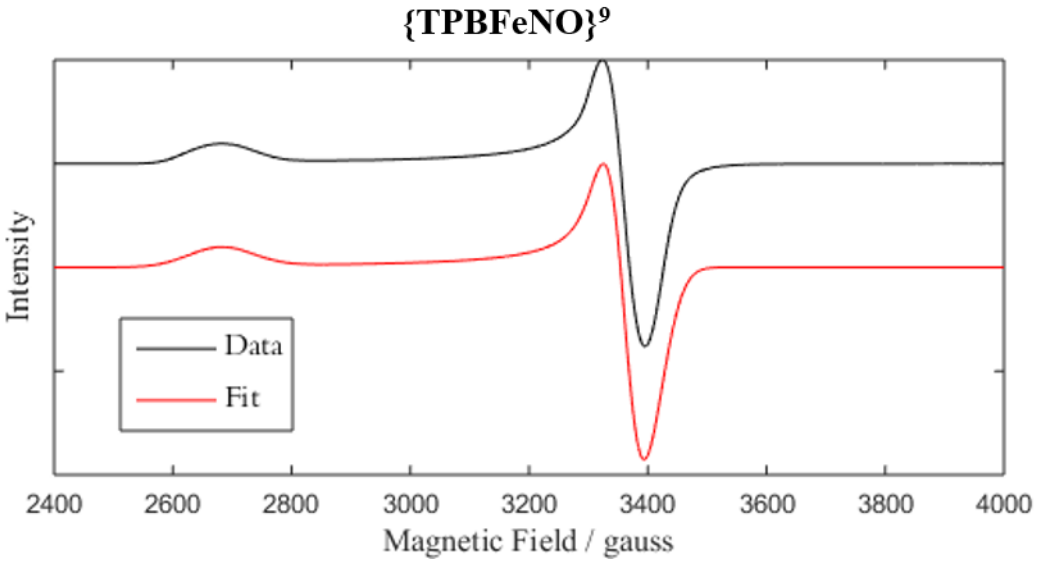
Compound	**{TPBFeNO}^{8}** *	**{TPBFeNO}^{9}**	**{TPBFeNO}^{10}** **
Chemical Formula	$C_{68}H_{66}FeNOB_2P_3F_{24}$	$C_{36}H_{54}FeNOBP_3$	$C_{58}H_{92}FeNO_9NaP_3$
Formula Weight	1539.63	676.41	1129.89
Crystal System	Monoclinic	Triclinic	Monoclinc
Space Group	$P2_1/c$	P-1	C2/c
a [Å]	20.1940(2)	10.8566(3)	34.611(2)
b [Å]	13.9917(8)	11.3808(4)	10.8164(7)
c [Å]	25.7210(14)	15.9526(5)	32.356(2)
α [°]	90	91.345(2)	90
β [°]	109.837(3)	95.217(1)	98.5813 (18)
γ [°]	90	118.023(1)	90
V [Å^3]	6836.2(7)	1727.84(10)	11977.5(13)
Z	4	2	8
D_{calcd} [g cm^{-1}]	1.496	1.300	1.253
F_{000}	3144.0	722.0	4848.0
μ [mm^{-1}]	0.400	0.605	0.393
Temperature [K]	100	100	100
Wavelength [Å]	0.71073	0.71073	0.71073
Measured Reflections	19288	29705	22866
Unique Reflections	127279	22786	14652
Data/Restraints/Parameters	12729/54/941	22786/0/593	14652/1316/928
R(F) (I>2σ(I))	0.0622	0.0353	0.0499
wR(F^2) (all)	0.1854	0.0790	0.1073
GOOF	1.037	1.030	1.013

* There is one highly disordered CF_3 group on the $BArF_{24}$ counteranion. Modeling this disorder led to no improvement in the **{TPBFeNO}^{8}** cation of interest, hence such disorder was not modeled.

** Both 12-crown-4 units that encapsulate the Na counteraction are rotationally disordered over two positions. As such, restraints (EADP and SAME) have been applied to the smaller component. No changes to the structural parameters of the **{TPBFeNO}^{10}** anion of interest occurred due to this process.

EPR Spectroscopy:

Figure S34: X-Band EPR spectrum of **{TPBFeNO}^{9}** in 2-MeTHF at 7 K and its simulation. The simulation was done using the least-squares fitting program of EasySpin[4] and produced the following parameters: g = [2.50048, 1.99439, 1.96918] and HStrain = [450.420, 159.384, 205.277].



DFT Calculations:

DFT Discussion: The calculated structures using BP86/def2-TZVVP (Fe, B, P, N, O); 631-G(d) (C, H) led to very good agreement with the experimental values as can be seen in **Table S4**. Higher spin states were also calculated and revealed poor matches to the experimental data (long Fe–P, Fe–N, and N–O bond distances) and bent Fe–N–O angles. They were also notably higher in energy. Attempts to generate broken symmetry solutions using BP86 with $S = 1$ NO^- antiferromagnetically coupled to an intermediate spin metal center led to collapse of the wavefunction to the low-spin solution. This is unsurprising because BP86 is a pure functional and as such will favor electron pairing. To find broken symmetry solutions we used B3LYP, which as a hybrid functional should favor such solutions. In these cases broken-symmetry solutions are found, which in all cases are of a similar energy to the standard low-spin calculation. However, these calculations despite using the same basis sets provide both a poorer estimate of the solid state structure and more importantly predict that the triplet ground state for **{TPBFeNO}^{8}** is more stable than the singlet ground state by 23.1 kcal mol^{-1} (**Table S4**). This triplet structure fails to capture the η^4-BCCP interaction that is characteristic of this molecule in the solid state and solution. Therefore we believe that these calculations do not provide as accurate a picture of the electronic structure of these molecules. As such only the BP86 calculations are discussed in the main text.

Table S3: A comparison of calculated (BP86, low-spin) and experimental bond parameters demonstrating good agreement between optimized gas-phase structures and experimental values from X-ray data for **{TPBFeNO}^{8}**, **{TPBFeNO}^{9}**, and **{TPBFeNO}^{10}**.

Metric	{TPBFeNO}^{8} Experimental	{TPBFeNO}^{8} Calculated	{TPBFeNO}^{9} Experimental	{TPBFeNO}^{9} Calculated	{TPBFeNO}^{10} Experimental	{TPBFeNO}^{10} Calculated
N-O	1.160(4) Å	1.177 Å	1.1901(7) Å	1.1915 Å	1.2207(16) Å	1.2110 Å
Fe-N	1.655(3) Å	1.649 Å	1.6712(5) Å	1.6555 Å	1.6505(13) Å	1.6426 Å
Fe-B	2.311(3) Å	2.314 Å	2.4451(6) Å	2.4121 Å	2.4455(16) Å	2.4530 Å
Fe-P	2.2774(9) Å	2.3053 Å	2.28169(18) Å	2.28327 Å	2.2125(4) Å	2.2297 Å
Fe-P	2.2777(9) Å	2.3085 Å	2.29654(19) Å	2.31773 Å	2.2155(4) Å	" "
Fe-P	2.2917(8) Å	2.3271 Å	2.34813(18) Å	2.35522 Å	2.2268(4) Å	" "
P-Fe-P	100.05(3) °	99.07 °	105.897(6) °	106.835 °	115.480(16) °	115.693 °
P-Fe-P	100.50(3) °	101.54 °	110.500(7) °	110.39 °	115.576(16) °	" "
P-Fe-P	153.72(3) °	153.14 °	125.833(7) °	126.19 °	115.644(15) °	" "
Fe-N-O	175.8(3) °	175.0 °	176.18(6) °	175.62 °	179.05(12) °	180.00 °
N-Fe-B	175.02(14) °	174.71 °	174.99(2) °	174.53 °	179.21(6) °	180.00 °
Σ (< C-B-C)	349.3(3) °	352.8 °	339.69(5) °	336.49 °	332.18(12) °	331.93 °

Table S4: Spin ladder energies for different functionals for **{TPBFeNO}$^{8\text{-}10}$**. Broken symmetry solutions in which an $S = 1$ NO^- unit is antiferromagnetically coupled to the metal are indicated by BS. In all cases attempts to find broken symmetry solutions with BP86 led to collapse of the wavefunction to the electron-paired, low-spin solution. The energies given are relative to the low-spin wavefunction for that functional and species.

Functional	Spin State	Species	Energy (kcal mol^{-1})
BP86	$S = 0$	**{TPBFeNO}^{8}**	0
BP86	$S = 1$	**{TPBFeNO}^{8}**	3.6
BP86	$S = 2$	**{TPBFeNO}^{8}**	27.5
B3LYP	$S = 0$	**{TPBFeNO}^{8}**	0
B3LYP	$S = 1$	**{TPBFeNO}^{8}**	-23.1
B3LYP	$S = 2$	**{TPBFeNO}^{8}**	-7.4
B3LYP	BS $S = 0$	**{TPBFeNO}^{8}**	1.5
BP86	$S = 1/2$	**{TPBFeNO}^{9}**	0
BP86	$S = 3/2$	**{TPBFeNO}^{9}**	28.9
BP86	$S = 5/2$	**{TPBFeNO}^{9}**	53.1
B3LYP	$S = 1/2$	**{TPBFeNO}^{9}**	0
B3LYP	$S = 3/2$	**{TPBFeNO}^{9}**	17.5

B3LYP	$S = 5/2$	**{TPBFeNO}^{9}**	34.5
B3LYP	BS $S = 1/2$	**{TPBFeNO}^{9}**	0.1
BP86	$S = 0$	**{TPBFeNO}^{10}**	0
BP86	$S = 1$	**{TPBFeNO}^{10}**	25.6
BP86	$S = 2$	**{TPBFeNO}^{10}**	53.4
B3LYP	$S = 0$	**{TPBFeNO}^{10}**	0
B3LYP	$S = 1$	**{TPBFeNO}^{10}**	4.6
B3LYP	$S = 2$	**{TPBFeNO}^{10}**	17.5
B3LYP	BS $S = 0$	**{TPBFeNO}^{10}**	1.8

Table S5: Calculated Mössbauer parameters for the spin ladder of **{TPBFeNO}$^{8\text{-}10}$**.

Species	Spin State	Isomer Shift (mm s^{-1})	Quadrupole Splitting (mm s^{-1})
{TPBFeNO}^{8}	$S = 0$	0.19	-1.48
{TPBFeNO}^{8}	$S = 1$	0.23	1.84
{TPBFeNO}^{8}	$S = 2$	0.35	-2.27
{TPBFeNO}^{9}	$S = 0$	0.17	0.87
{TPBFeNO}^{9}	$S = 1$	0.33	1.53
{TPBFeNO}^{9}	$S = 2$	0.47	-2.04
{TPBFeNO}^{10}	$S = 0$	0.10	1.68
{TPBFeNO}^{10}	$S = 1$	0.33	1.05
{TPBFeNO}^{10}	$S = 2$	0.51	-0.44

Figure S35: The gas-phase optimized geometry of **{TPBFeNO}^{8}** (BP86, *S* = 0) with hydrogens omitted.

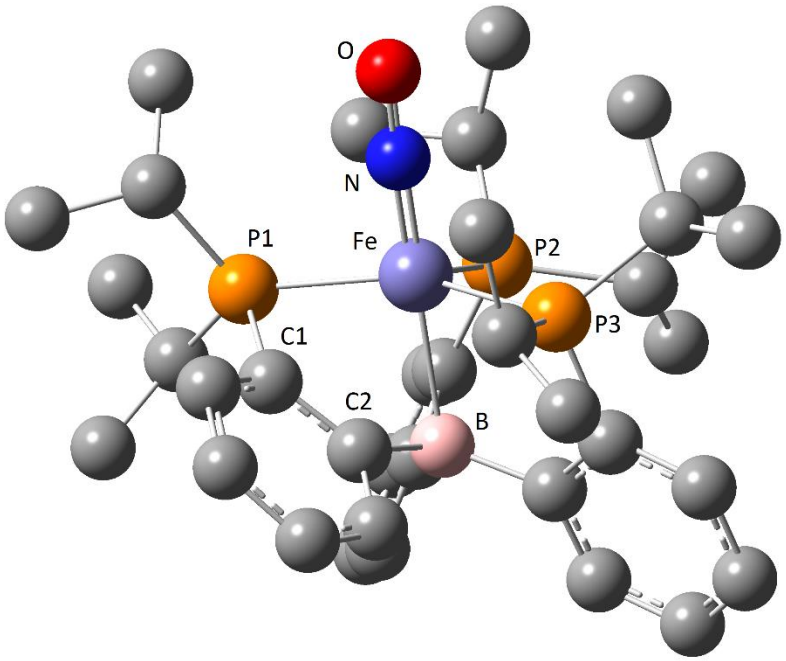


Table S6: Optimized coordinates for **{TPBFeNO}^{8}** (BP86, *S* = 0).

Fe	-0.05524358	-0.57418801	0.56542132
P	-2.21095562	-1.14750866	-0.02892657
P	-0.36714006	1.66118293	1.03471327
P	2.25854979	-0.68484454	0.34319089
C	0.81375958	-1.55286359	-2.77021260
C	2.72969517	-2.45146118	-0.12114075
C	1.62568855	1.05661428	-1.71027320
C	-0.06720730	-0.97335335	-1.79150101
C	-3.57281644	-0.27844223	-1.00604717
H	-3.10817419	0.68697864	-1.26068684
C	-0.98408312	1.69887757	-1.56742057
C	-1.37957644	2.04888845	2.58664883
C	2.70322002	-3.42739650	1.07408974
C	-1.02112898	-1.87784593	-1.18400757
C	3.33083908	-0.15088248	1.80983697
C	0.72803127	-2.88346013	-3.16441707
N	-0.08612628	-1.48740479	1.93790098
C	2.72135834	0.44134992	-1.03511371
C	-0.15317610	-3.76261657	-2.48987112
C	-1.57072840	2.14763081	-2.77257084
C	-2.94548086	-2.56193294	0.96421389
H	-2.05065247	-3.18662742	1.15302187
C	-2.88375258	1.76796599	2.43263456
C	-0.99180294	-3.27199351	-1.49580014

C	4.04987302	0.77594547	-1.37632409
C	-1.30495079	2.38324199	-0.36920152
C	-2.46796304	3.23070501	-2.77402062
C	2.72733299	-0.53748026	3.17578565
C	-2.18443238	3.48417691	-0.36907600
C	-2.77439903	3.89848588	-1.57532086
C	-3.48608248	-2.09942236	2.33593384
H	-2.73572780	-1.54445405	2.92152286
H	-3.77713237	-2.98723514	2.92602589
H	-4.38357547	-1.46712212	2.22959564
B	0.12668786	0.56539270	-1.43980220
C	1.92180371	2.03882362	-2.68336839
C	3.24401177	2.37892462	-3.01203250
C	-4.00400001	-3.42977674	0.24408488
H	-4.19377660	-4.33196363	0.85421140
C	4.81711455	-0.57774173	1.77866053
C	-3.89899922	-1.00714280	-2.32785543
C	-0.87451052	1.34008863	3.86016670
C	4.31127210	1.73797611	-2.36523402
C	1.70667810	3.00328648	2.61051977
C	1.11613353	2.85966421	1.19288090
C	4.02822364	-2.59304860	-0.94121970
C	-4.84951611	0.01521981	-0.19152670
C	0.82038836	4.26493279	0.62815999
O	-0.13182719	-2.05318274	2.96952818
H	-3.69806846	-3.76327135	-0.76038259
H	-4.96544772	-2.90094157	0.14272573
H	-5.42346947	-0.89702388	0.03955243
H	-4.64596332	0.54627198	0.75107954
H	-5.50485005	0.66459962	-0.79977999
H	-4.36437363	-1.99280978	-2.16047704
H	-4.62067806	-0.39232505	-2.89679543
H	-3.00530229	-1.14703894	-2.95726757
H	-1.34024949	1.63651476	-3.71569197
H	-2.93033482	3.55639349	-3.71268180
H	-3.46876366	4.74556714	-1.57880964
H	-2.41141362	4.02867652	0.55424082
H	-1.05450173	0.25349191	3.80428409
H	-1.43615556	1.72047004	4.73309066
H	0.19390676	1.49860718	4.06358471
H	-1.23841319	3.14300052	2.70802075
H	-3.33600679	2.27143698	1.56498359
H	-3.41415789	2.11129174	3.34004237
H	-3.06685062	0.68361491	2.34014863
H	1.02072588	3.54240077	3.28725882
H	1.96849865	2.04391174	3.08249624
H	2.63260369	3.60421643	2.54827330
H	1.87679329	2.39617033	0.53962702
H	0.00656463	4.77094601	1.17939355
H	0.55317160	4.24558030	-0.43889932
H	1.72660013	4.88829500	0.74134481

H	1.09555115	2.54119255	-3.20019020
H	3.44089485	3.14106499	-3.77428086
H	5.34691398	1.99011501	-2.61693473
H	4.89545747	0.29334329	-0.88097264
H	3.34540947	-0.09714188	3.97982612
H	1.69773155	-0.17098578	3.30408047
H	2.71980359	-1.62931224	3.33050364
H	3.29834634	0.95085787	1.71676243
H	5.33261338	-0.09492113	2.62927866
H	4.93723014	-1.66614689	1.90347682
H	5.35043031	-0.27427222	0.86606682
H	3.53622135	-3.25788756	1.77645272
H	1.75920180	-3.38238255	1.64088182
H	2.80853059	-4.45880476	0.69081969
H	1.89388642	-2.73031866	-0.78651993
H	4.11622327	-3.64033214	-1.28517321
H	4.02950120	-1.94639949	-1.83373365
H	4.92941899	-2.36730887	-0.34734254
H	1.53415075	-0.89573937	-3.26686128
H	1.35320686	-3.25525570	-3.98357983
H	-0.19059374	-4.82348243	-2.76052400
H	-1.66627383	-3.96235673	-0.98359228

Figure S36: The gas-phase optimized geometry of **{TPBFeNO}^{8}** (BP86, *S* = 1) with hydrogens omitted.

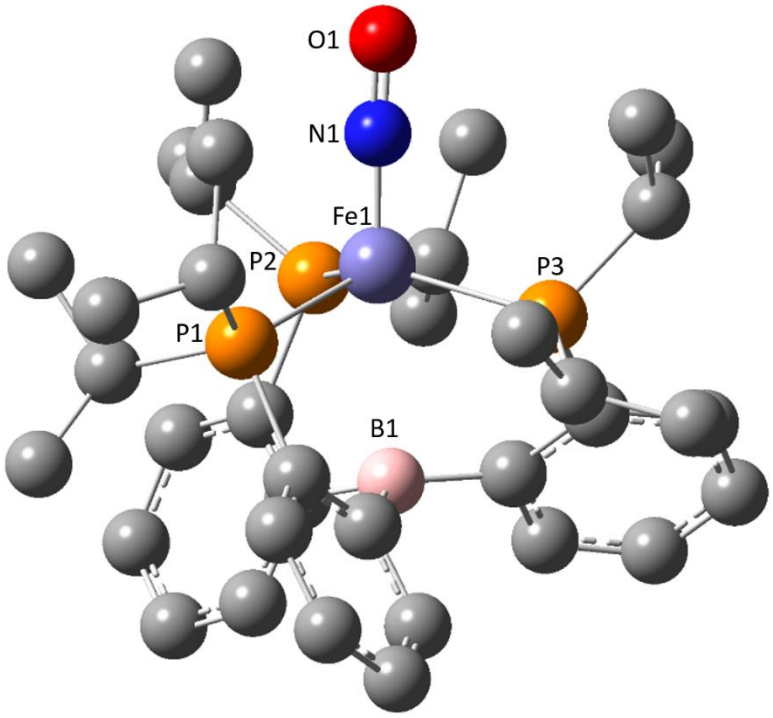


Table S7: Optimized coordinates for **{TPBFeNO}^{8}** (BP86, *S* = 1).

Fe	-0.30939850703205	-0.06826246300627	1.04952039816710
P	-1.68994233595370	-1.57777129899623	-0.17355095303706
P	-0.35989508127107	2.31285954571190	0.99577247754068
P	1.91133938914158	-0.79486581602667	0.74313644684231
C	0.53325389193045	-1.08660232894666	-3.57569291346197
C	2.09876504183547	-2.50026677163984	-0.04399341901248
C	1.65570243727361	0.95334304907603	-1.41901126437319
C	-0.11623372470787	-0.86675549786931	-2.33723332932919
C	-3.36644790819307	-0.74969565878595	-0.44689998612055
H	-3.05684409883624	0.29088634787307	-0.65888043452089
C	-0.96420968276935	1.63944094780204	-1.65352754813300
C	-1.51620604205099	3.10190854505536	2.24784303958103
C	1.81978683575299	-3.63208062584397	0.96514270661157
C	-0.99237993482579	-1.87599159697300	-1.85031983545171
C	3.09591327974569	-0.68467064122691	2.21685146073617
C	0.30912460140464	-2.25143254458211	-4.32631029842588
N	-0.70273282300262	-0.35900633587498	2.63172334375636
C	2.58525921335900	0.38823006239316	-0.49879149475236
C	-0.54983129262553	-3.24148420942237	-3.83126304284369
C	-1.69123513545450	1.77889010601572	-2.86313247996449
C	-1.96263462373890	-3.30338200604155	0.55465538929279
H	-1.06312610926478	-3.83754753533810	0.19275762905787
C	-2.90670999224661	2.44219571681575	2.24102995764276
C	-1.18842923013026	-3.05749071332953	-2.59423725873342
C	3.92493056020489	0.82708547222048	-0.50042290453717
C	-1.17819744159586	2.61561746129891	-0.63087393450733
C	-2.55793029799410	2.86104228343176	-3.08383993148892
C	2.39732449287370	-1.01866147053397	3.55025213259364
C	-2.06627262426901	3.68530957538790	-0.85304830973810
C	-2.74255083583626	3.81926110736061	-2.07829841866727
C	-1.93308208307255	-3.31239804949020	2.09572564072166
H	-0.98996207535951	-2.91622316591083	2.49985953700379
H	-2.04220282522358	-4.35155158284295	2.45347266032375
H	-2.76154335759274	-2.72654051209580	2.52666325570883
B	0.14394102867138	0.50935985956936	-1.59641351403480
C	2.12545476157548	1.93960942320512	-2.32310119423231
C	3.47017377427711	2.34203028741464	-2.34180038658897
C	-3.21009490353816	-4.07780405306941	0.06800708505228
H	-3.12236567950688	-5.12703563895627	0.40196342254116
C	4.42377917095292	-1.46919963596002	2.11549182706364
C	-4.16970745023515	-1.24489896166901	-1.66456035279963
C	-0.93207889934487	3.12140931348428	3.67526031507105
C	4.37092780795347	1.78849232128658	-1.42180667111462
C	2.14733307236074	3.17079257868986	2.11676652199814
C	1.16872892532872	3.41850823562016	0.95217642659691
C	3.38724559700695	-2.75285278290521	-0.85058306530522
C	-4.21961904571686	-0.73796939179914	0.83774806105291
C	0.84230899086503	4.91490894479125	0.79377359236659
O	-1.02858213198476	-0.52372466298915	3.75219534663960

H	-3.34074286567431	-4.08731633616745	-1.02383532376285
H	-4.13398870653291	-3.67411717232026	0.51158924328676
H	-4.65654283445514	-1.72673773372964	1.05024684372547
H	-3.64571725325519	-0.42072532263299	1.72348365219333
H	-5.05884587252843	-0.03127371118807	0.71332484308088
H	-4.57713093866228	-2.25655010737616	-1.51156334620640
H	-5.02632995818529	-0.56611084732069	-1.82554541879433
H	-3.56639625182906	-1.24948333987548	-2.58609278650996
H	-1.55719325810448	1.02998382686275	-3.65125116256855
H	-3.09369251065327	2.94829936988894	-4.03442644339981
H	-3.42293825193019	4.66236269873964	-2.23344598446386
H	-2.25307379235138	4.42527014061121	-0.06897069030033
H	-0.65685958378991	2.11295803000274	4.02514147375237
H	-1.69631682926776	3.51356602934353	4.36924798872023
H	-0.04813663114751	3.77035548174544	3.76097164449697
H	-1.62475451516632	4.15086011354157	1.91261911877602
H	-3.34574963142327	2.38467189012911	1.23191699805459
H	-3.59306889045676	3.03035839892153	2.87551665522975
H	-2.86272446513167	1.42438795421929	2.66133210542149
H	1.84621378371638	3.70154224541389	3.03365112970407
H	2.23736754757611	2.10050511396632	2.36189883667345
H	3.14850911122134	3.54128484339503	1.83647120386468
H	1.65412927682920	3.07195805035558	0.02381488512830
H	0.36691089019131	5.33303287199092	1.69783787291246
H	0.18902146656844	5.11256704358308	-0.07180286872384
H	1.78190528567757	5.47309632447330	0.63344369756713
H	1.41903002948452	2.40409490426526	-3.02062082146644
H	3.80541656678180	3.09863248369677	-3.05840379337223
H	5.41820723254883	2.10606082083756	-1.41044692663501
H	4.64001791149848	0.42905700132100	0.22298197805941
H	3.12774330363290	-0.93507074475590	4.37446220385250
H	1.56890729248651	-0.32975750187931	3.76784273988452
H	2.00270611007348	-2.04874930096158	3.56383411629914
H	3.34325470090448	0.39334753935917	2.22742550979575
H	5.07718347516098	-1.15927750724933	2.95055285745480
H	4.26525630854000	-2.55463500252844	2.21601124155160
H	4.97653165764267	-1.29629398756552	1.18007310836946
H	2.65444474784978	-3.77441434736308	1.67022660073334
H	0.90631344410121	-3.45237307663312	1.55621236112928
H	1.68862411029571	-4.58505136852532	0.42230495182189
H	1.26440049018544	-2.48360781710024	-0.76786878077401
H	3.26402783070721	-3.68343235637211	-1.43321850809323
H	3.59590927768033	-1.93862380349204	-1.56272387513186
H	4.26894222473470	-2.88570942310444	-0.20502554310623
H	1.23387828568287	-0.33335687257370	-3.95329924391982
H	0.82179631467262	-2.39261602128381	-5.28308507273467
H	-0.71644735497810	-4.16438330966055	-4.39527029307636
H	-1.82740177006185	-3.85706846738300	-2.21415160128827

Figure S37: The gas-phase optimized geometry of **{TPBFeNO}^{8}** (BP86, *S* = 2) with hydrogens omitted.

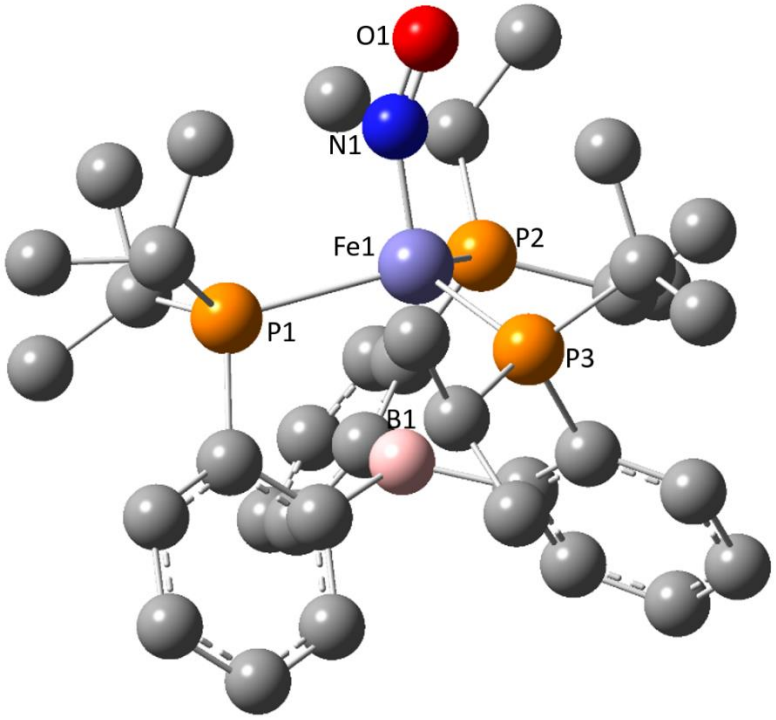


Table S8: Optimized coordinates for **{TPBFeNO}^{8}** (BP86, *S* = 2).

Fe	-0.16929555059575	-0.00033987118195	1.02206701301077
P	-1.74712856156698	-1.55276876161934	-0.15488860525650
P	-0.49498906341419	2.38803762011708	0.99895243393945
P	2.08256177711008	-0.88114434648506	0.70049676011602
C	0.62906407106170	-1.10505439887358	-3.43815402375595
C	2.20043572006663	-2.56344213274138	-0.13039762269211
C	1.67553751943384	0.98381406455369	-1.32837947743436
C	-0.07594978013065	-0.86438879577937	-2.23334118989596
C	-3.41225310448854	-0.71300564635872	-0.42537105993684
H	-3.09777464832229	0.32742925481565	-0.63145599901673
C	-0.95646122917949	1.63839240663365	-1.63610664304085
C	-1.68455049932628	3.17730607960526	2.21278962563799
C	1.91445872910996	-3.71312582482101	0.85646673366560
C	-1.00705198487941	-1.85237430769684	-1.80249682768715
C	3.25808173920836	-0.80809653754690	2.17426643956745
C	0.40824723650071	-2.25991971216047	-4.20438105068052
N	-0.84522492022627	-0.28067089591938	2.64446935658408
C	2.67107078076885	0.37290118380229	-0.50584350527071
C	-0.51516644117672	-3.22140300450800	-3.76777879560014
C	-1.62489491415473	1.74697131964088	-2.88226627439520
C	-2.01026958144490	-3.27473375383310	0.58551187835310
H	-1.11750168794536	-3.80794561212697	0.20497257103272
C	-3.05449110991682	2.47627587230984	2.20071744350666

C	-1.21202976236492	-3.02092349313482	-2.56656137747063
C	4.01196005413698	0.80530870382179	-0.56560715004451
C	-1.24753512382877	2.63477644460415	-0.65268291237622
C	-2.50238212095846	2.80510801596091	-3.16555542313621
C	2.54433654520501	-1.22473969074069	3.47780727930555
C	-2.13875154678519	3.68911523429658	-0.93639374415991
C	-2.75626616291984	3.78407524095603	-2.19372071551602
C	-1.93801747387027	-3.27012988905692	2.12633064237506
H	-0.98631659950933	-2.86109348267797	2.49929388513740
H	-2.02930395516454	-4.30635184347101	2.49789380810039
H	-2.75621047480269	-2.68370738984534	2.57573152178563
B	0.15315630845622	0.50695156832213	-1.46021373782900
C	2.09924617845045	2.02364732881745	-2.19703463665917
C	3.44052409078087	2.43013660718817	-2.27240450344255
C	-3.26159508166277	-4.05804665749195	0.12705901922135
H	-3.17424509730164	-5.10031185869935	0.48302392962584
C	4.60047781215894	-1.56080349233672	2.04254756764491
C	-4.20835811762779	-1.20467834288804	-1.64863984710520
C	-1.12497058919432	3.26161623766623	3.64791971932580
C	4.40094261597191	1.82253043320307	-1.45066004496866
C	2.02902123279846	3.10933778414835	2.15674945395585
C	1.05583521383365	3.45347702013826	1.01290648086335
C	3.48154822400739	-2.80108434698241	-0.95249021048891
C	-4.26545560525671	-0.71059357121999	0.85947223285364
C	0.75215142749956	4.96129727979058	0.93710731781163
O	-0.75499418995311	-0.32322767417136	3.83370755775873
H	-3.39380277960217	-4.09094116203542	-0.96475150911061
H	-4.18333218901940	-3.64332451420400	0.56466741848880
H	-4.71602438315211	-1.69702054431081	1.05310076880561
H	-3.68514195288064	-0.41984266489648	1.75004720084871
H	-5.09485553208378	0.00957560190782	0.74749516265905
H	-4.60481318698992	-2.22224812701100	-1.50408378769316
H	-5.07153159395178	-0.53326817710574	-1.80653634773234
H	-3.60149191459847	-1.19537479463916	-2.56798380843143
H	-1.43633460022980	0.98886684619974	-3.65016091450428
H	-2.99097380371267	2.86241228925483	-4.14366143090882
H	-3.44254305283519	4.61041032567062	-2.40286013617916
H	-2.37180681127751	4.44222552701423	-0.17710610145878
H	-0.84061905638878	2.27303154411198	4.04276312018708
H	-1.90823006876295	3.66873736886076	4.31135508360588
H	-0.25457107389818	3.93074036970175	3.72290316618306
H	-1.81511660542513	4.21112384185327	1.83873090576134
H	-3.47448576575232	2.38494653169344	1.18588699542400
H	-3.76739071222142	3.05803907293945	2.81114433463788
H	-2.98347041600160	1.46910526129175	2.64214790956402
H	1.67221012375356	3.46142969351395	3.13720247194305
H	2.20384578404850	2.02317810449888	2.23211800133379
H	3.00189020089867	3.59415203688330	1.96371948671982
H	1.53257859056263	3.15089887748409	0.06443263792221
H	0.29743308852396	5.34266905427877	1.86703068717947
H	0.08760661295216	5.20922762579143	0.09270750711332

H	1.69801156968513	5.51133780728183	0.78635182194333
H	1.35469007814471	2.52122776558798	-2.82832299171249
H	3.73147714775594	3.22859999386151	-2.96278006587791
H	5.44735616705633	2.14050809053160	-1.48890237101123
H	4.76815820194128	0.35860564119261	0.08466316886096
H	3.24187616062616	-1.11002835578821	4.32630790805500
H	1.65520723349724	-0.61174251566978	3.68756876313567
H	2.23094778975125	-2.28200439933957	3.45148940766066
H	3.47791579225492	0.27509471113888	2.23545489093379
H	5.23739873166397	-1.29427127231478	2.90474425247548
H	4.45754572356746	-2.65293044048878	2.07114694279460
H	5.16187093703054	-1.31827777738291	1.12739416406122
H	2.74500508521258	-3.87055360200896	1.56359321646968
H	0.99609946954596	-3.54516904816198	1.44430487679762
H	1.78579021852860	-4.65298889276697	0.29119537838001
H	1.35831128159328	-2.50972161883689	-0.84350949205333
H	3.35078386301861	-3.71887488823537	-1.55302549800074
H	3.68339688856978	-1.97200669405408	-1.64947491317773
H	4.36774089774864	-2.94617844303642	-0.31542034728910
H	1.36589483769796	-0.36940691084547	-3.78014873260970
H	0.96475024296309	-2.41349496472695	-5.13469958974589
H	-0.68752489670965	-4.13128795731996	-4.35098248119302
H	-1.90751141169032	-3.79305365338821	-2.22910931457439

Figure S38: The gas-phase optimized geometry of **{TPBFeNO}^{8}** (B3LYP, *S* = 0) with hydrogens omitted.

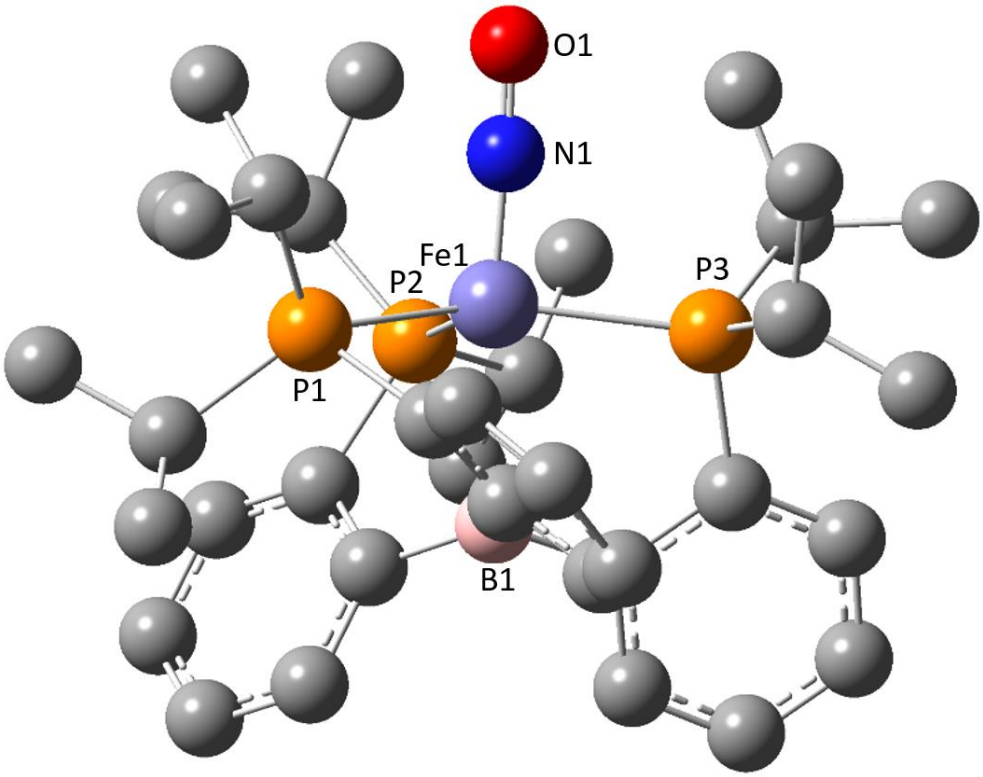


Table S9: Optimized coordinates for **{TPBFeNO}^{8}** (B3LYP, *S* = 0).

Fe	-0.04819828707438	-0.57493765021221	0.60798111618462
P	-2.21185679807510	-1.17574090240280	-0.02942909573720
P	-0.36813244708627	1.70558722060026	1.03092213638432
P	2.29072038023742	-0.68532319415641	0.37799647394567
C	0.78975901399165	-1.54990017202614	-2.79097455562327
C	2.74980628695929	-2.44059730761125	-0.11647007467661
C	1.64901862808137	1.03184104627610	-1.69960429744629
C	-0.08535191804761	-0.98370734284648	-1.81154394113052
C	-3.59055376767885	-0.29787395830454	-0.96834251307269
H	-3.14045919677018	0.66363923156288	-1.21796944705696
C	-0.96197598078561	1.68322376176924	-1.57934119981065
C	-1.38725449004871	2.10000051885667	2.56881059823779
C	2.69447107103345	-3.43689706808626	1.05757692253547
C	-1.06558632000108	-1.87221127187551	-1.25326821215605
C	3.37561987840960	-0.16672655475341	1.83249746230282
C	0.68347645018100	-2.85939200759221	-3.22439653903585
N	-0.07839792586460	-1.47941193002850	1.97259277188585
C	2.73588785288200	0.44579019527496	-0.99944216444487
C	-0.23457909694031	-3.72483100315124	-2.60642605070424
C	-1.55135591603467	2.09829041830237	-2.78591826831652
C	-2.93399381474103	-2.60667940265198	0.94148269647973
H	-2.04844812009843	-3.23335495898873	1.11002923579759
C	-2.89073440526491	1.81966585767589	2.42888489992716
C	-1.07599192976482	-3.24106511978407	-1.61960018583560
C	4.05482901185489	0.80869830008528	-1.31547203123861
C	-1.28681095989066	2.38292610430084	-0.40042638392642
C	-2.45152068191720	3.16782485164546	-2.81196366982019
C	2.76747386696128	-0.53801375501463	3.19825383768425
C	-2.17253306691110	3.46894823346045	-0.42764096132737
C	-2.76205208258280	3.85378726374510	-1.63421297560016
C	-3.44978749739275	-2.15690950659882	2.32489207748437
H	-2.70187178224310	-1.59945304969341	2.89394699920177
H	-3.71650182447528	-3.04330167954815	2.91225649007775
H	-4.34946226589614	-1.53968718913492	2.24008289403501
B	0.14480085245521	0.54975316997955	-1.46522802581143
C	1.94507628290481	2.00227650630274	-2.67388829228599
C	3.25903403032431	2.36184272666131	-2.98117642818330
C	-4.01074286406691	-3.46782373630372	0.24720020856785
H	-4.17836784349810	-4.36945634093482	0.84867085589536
C	4.85189459555355	-0.61779177853116	1.81210881297954
C	-3.95489494331682	-0.99612353438666	-2.29285854242973
C	-0.88352115679127	1.39801041050369	3.84460491855627
C	4.31836480201805	1.75759205801661	-2.30527611119103
C	1.72213376840926	3.02172473230294	2.59028067913431
C	1.10265975612955	2.90550426230263	1.18542883615575
C	4.05436637759556	-2.59298150567193	-0.91902221611994

C	-4.85170979282856	-0.01223498938505	-0.13181780927197
C	0.79447611519578	4.32120401451957	0.66204357143507
O	-0.12879887775973	-2.01424619460538	3.00458205035047
H	-3.74092474872791	-3.78915373197225	-0.76145635279561
H	-4.96785403810523	-2.94384145481392	0.18211187239855
H	-5.42640622308234	-0.91750477746894	0.08147260305533
H	-4.63357166681765	0.48716157117373	0.81412653066278
H	-5.50327313108278	0.65361584167157	-0.70986423317408
H	-4.41191508229192	-1.97776305977053	-2.13495903747453
H	-4.68652347386316	-0.37530133201334	-2.82436997576931
H	-3.08766678435028	-1.12190174500632	-2.94666167822737
H	-1.31958209404430	1.57432724900728	-3.71113649474966
H	-2.91173300480527	3.46652154855132	-3.75030379113969
H	-3.45773995946262	4.68805217027609	-1.65453454460267
H	-2.40626997005861	4.02302462318518	0.47696078312648
H	-1.06367786683951	0.32005894778119	3.79685528192764
H	-1.44036126808552	1.78362029668227	4.70719391103548
H	0.17617264915134	1.55401198118539	4.04643726703994
H	-1.25297865225136	3.18424176745286	2.69171433905733
H	-3.34194768355326	2.28889201026455	1.55321413337163
H	-3.40981729509273	2.19896339680919	3.31764703294657
H	-3.08008248099302	0.74324006576588	2.38094582965666
H	1.06107632335872	3.55431593186158	3.28213640150157
H	1.97853838664727	2.06054738527627	3.03907577439784
H	2.64651107772658	3.60742023894873	2.51788634199084
H	1.85047554357909	2.46853202369806	0.51695046721893
H	-0.00803331669337	4.80556367046504	1.23165282091032
H	0.51649573981467	4.32883162547609	-0.39334370753359
H	1.69183302225124	4.94115171319246	0.77797181413341
H	1.12939687630537	2.48218607254037	-3.20814956278371
H	3.45330259459333	3.11108612064492	-3.74413419381998
H	5.34551875945339	2.02728465191882	-2.53440775899531
H	4.89285729284734	0.36048170929911	-0.79680886492345
H	3.38970634806659	-0.11105728160700	3.99409769355752
H	1.75341654610555	-0.15650767667956	3.32777143706905
H	2.74039736750878	-1.62084959188685	3.35327502157764
H	3.36520872182990	0.92575865152010	1.74159273176266
H	5.37116473083361	-0.12979557554224	2.64579705963466
H	4.95121625834917	-1.69659877346030	1.95956852989578
H	5.38758928835356	-0.34916566957931	0.90074328173540
H	3.51162955738851	-3.29023075058038	1.76985811412118
H	1.74988134175523	-3.39081620799611	1.60671533738893
H	2.79300842584774	-4.45430170702067	0.66048030137726
H	1.92912844173319	-2.69966039200344	-0.79185209142642
H	4.12679211865841	-3.62691203762891	-1.27851002173673
H	4.08147542376159	-1.93592097734873	-1.79260503693093
H	4.94423169952538	-2.39733677123832	-0.31394160581086
H	1.53403953786343	-0.90808887336880	-3.24934488736412
H	1.32030041723310	-3.22087125189022	-4.02720648468601
H	-0.29718191940691	-4.76674518643545	-2.90858776748258
H	-1.77280358826540	-3.92349128920062	-1.14990806411017

Figure S39: The gas-phase optimized geometry of **{TPBFeNO}^{8}** (B3LYP, *S* = 1) with hydrogens omitted.

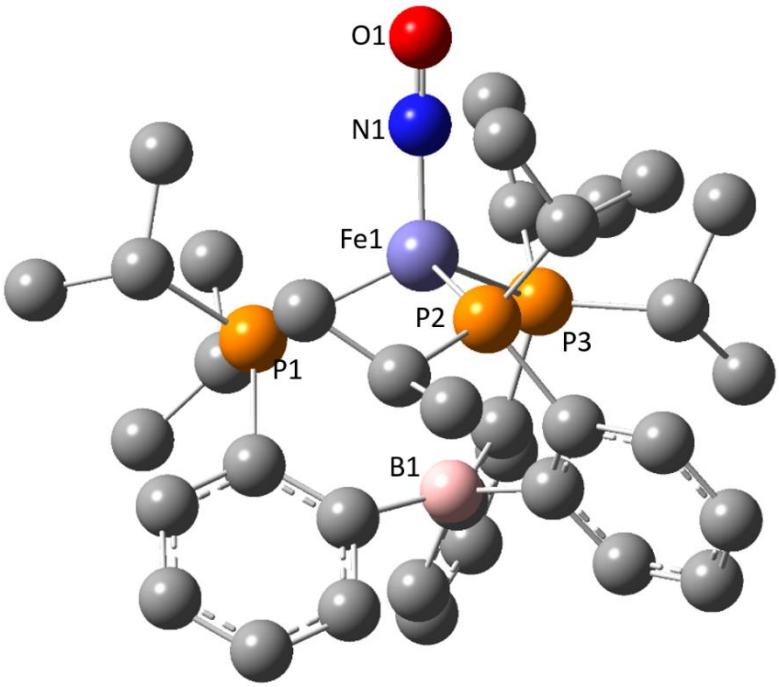


Table S10: Optimized coordinates for **{TPBFeNO}^{8}** (B3LYP, *S* = 1).

Fe	-0.24025414438437	-0.22019766733440	1.34379885335955
P	-1.84705574139152	-1.52822271570018	-0.15859422445461
P	-0.45650422067295	2.25159102425507	1.07627937741691
P	2.12010185991180	-0.78833490388679	0.69872726194201
C	0.65430302532435	-1.18957001554848	-3.42609418666062
C	2.24408192737394	-2.49579410219217	-0.07731060563089
C	1.73482343036572	0.98064569392442	-1.46335516974045
C	-0.06409263543180	-0.87979414900404	-2.25234451884495
C	-3.47912021188424	-0.67159751212346	-0.52464729762783
H	-3.14745292328717	0.35713956065007	-0.70762095638799
C	-0.90809107907211	1.63293833791693	-1.63887616513400
C	-1.64476566286281	3.05527511761255	2.28368075307066
C	1.93559552452115	-3.60326885044124	0.94796767518894
C	-1.02722043528235	-1.81669519471777	-1.78801605339293
C	3.37081656849307	-0.65111892574044	2.10665887254599
C	0.41163373007800	-2.35443820037134	-4.15651047423444
N	-0.63495888806933	-0.42506524012280	3.02942901032878
C	2.69495107945761	0.39859787984103	-0.59106988729234
C	-0.53480050384957	-3.26481808989926	-3.69458991321286
C	-1.58474704666714	1.78938708312363	-2.86700103460037
C	-2.17155604885565	-3.26176014910069	0.52330764085687
H	-1.28346338112141	-3.80876382749674	0.17962545864831
C	-3.00742062736188	2.34520515839259	2.30377325831674
C	-1.23174940182369	-3.00096386119884	-2.51238332256889

C	4.02619624701898	0.83683780239771	-0.64885150333664
C	-1.21215187332739	2.54016891079677	-0.58544460336049
C	-2.49118254540660	2.83026250362073	-3.08416776726827
C	2.72345761525587	-0.96035497384250	3.47037540785529
C	-2.14419702061411	3.56255014036508	-0.81028311674838
C	-2.76903939097435	3.72139041237094	-2.05167819674518
C	-2.15931558172412	-3.28138128134136	2.06448788136619
H	-1.21365602539217	-2.92197963348921	2.47746240803074
H	-2.30763876276972	-4.31028010732206	2.41378653661608
H	-2.96410384526422	-2.67167874634573	2.48908526264242
B	0.22980040822283	0.54436271826163	-1.64755174853195
C	2.16761818849353	1.98378572227194	-2.35493466718167
C	3.50391894969994	2.38574585879110	-2.42348501139372
C	-3.42021295361279	-4.01669201537004	0.01921296064422
H	-3.35433174533995	-5.06049604320893	0.34873328261608
C	4.68814625884048	-1.44212787547874	1.97183935147102
C	-4.22635607848512	-1.13976737298553	-1.78420167372642
C	-1.07281733017419	3.14294809451981	3.71148617952228
C	4.43594872590526	1.81070169728288	-1.56396891984931
C	2.04727332762343	3.10743819460692	2.18769546446689
C	1.05435827863649	3.37445097066889	1.04196706754685
C	3.51058029731340	-2.80423475898852	-0.89380138755243
C	-4.40107830637825	-0.65342439537539	0.70924584312540
C	0.73291357757859	4.87280757537723	0.91645161246308
O	-0.91621599831995	-0.49521718032268	4.16815783767711
H	-3.53484629156770	-4.02226895444092	-1.06657574376512
H	-4.33811025052769	-3.60377854198670	0.44637871410703
H	-4.87481129209019	-1.62432031725523	0.87937029237954
H	-3.87352489336493	-0.36872695120059	1.62422506122948
H	-5.20490499404857	0.07492484330813	0.55074614253580
H	-4.64103524188554	-2.14555574700594	-1.67136908700779
H	-5.06655259843053	-0.45978146866491	-1.97113838441813
H	-3.58656564651052	-1.12904104444053	-2.67126010933665
H	-1.38697567268011	1.08830944196620	-3.67401492754761
H	-2.98334347174023	2.93098941619349	-4.04751601393849
H	-3.47958917928878	4.53033158378363	-2.19721282117702
H	-2.40483046799963	4.25223072103945	-0.01457884501919
H	-0.77417546811702	2.16404220128086	4.09913532170888
H	-1.84775521160104	3.53629211190767	4.38020244613098
H	-0.21556731636908	3.81660272871960	3.77860264822064
H	-1.79298597259375	4.08165043170452	1.92723733959145
H	-3.44665478592268	2.24253824229799	1.30702669077283
H	-3.70918969962318	2.91957597521259	2.92027530685152
H	-2.92129785763645	1.34861603821946	2.74863546201445
H	1.72404955841006	3.55533241711525	3.13144437941742
H	2.19674812840309	2.03794408911010	2.36279999106199
H	3.02002025075076	3.54672314596698	1.93586414934955
H	1.53864745082202	3.05882458237480	0.11220481003084
H	0.26563847957825	5.27104885766002	1.82405207516772
H	0.07621845220916	5.08632633463445	0.06714495172561
H	1.66366703439192	5.43185977471978	0.76087318317867

H	1.44149255979754	2.46094540501820	-3.00898499090904
H	3.80494050336617	3.15450540339368	-3.12982293649604
H	5.47664220618920	2.12174193836117	-1.58978544935429
H	4.76693031922670	0.42889238378206	0.02848127445196
H	3.47038957741544	-0.83178090209709	4.26288986753574
H	1.88514354486119	-0.29568360330486	3.69085342355747
H	2.36024996786007	-1.99237049758452	3.52697081800928
H	3.61865347080611	0.41741875624021	2.09419134662100
H	5.36568275488917	-1.13269182486915	2.77685239515886
H	4.52602287595166	-2.51814001065729	2.08512245993365
H	5.20746412353868	-1.28148220608104	1.02438650961510
H	2.74737428257008	-3.73654406844763	1.66967074215444
H	1.01653607545476	-3.40586382473831	1.51185853026264
H	1.80757427029994	-4.55884155245836	0.42550537087865
H	1.41057180700815	-2.46818670266810	-0.78723421379882
H	3.34663253268385	-3.72398605785504	-1.46882989950701
H	3.74402009083048	-2.00659826053664	-1.60561304865519
H	4.38662603331931	-2.96823191190269	-0.26139962177184
H	1.41686798867356	-0.49893448000693	-3.77673695626849
H	0.97246327301946	-2.55405006074531	-5.06538406127242
H	-0.72626131060104	-4.18616776958455	-4.23755617564538
H	-1.93581539004161	-3.74429980357653	-2.16085816000542

Figure S40: The gas-phase optimized geometry of **{TPBFeNO}^{8}** (B3LYP, *S* = 2) with hydrogens omitted.

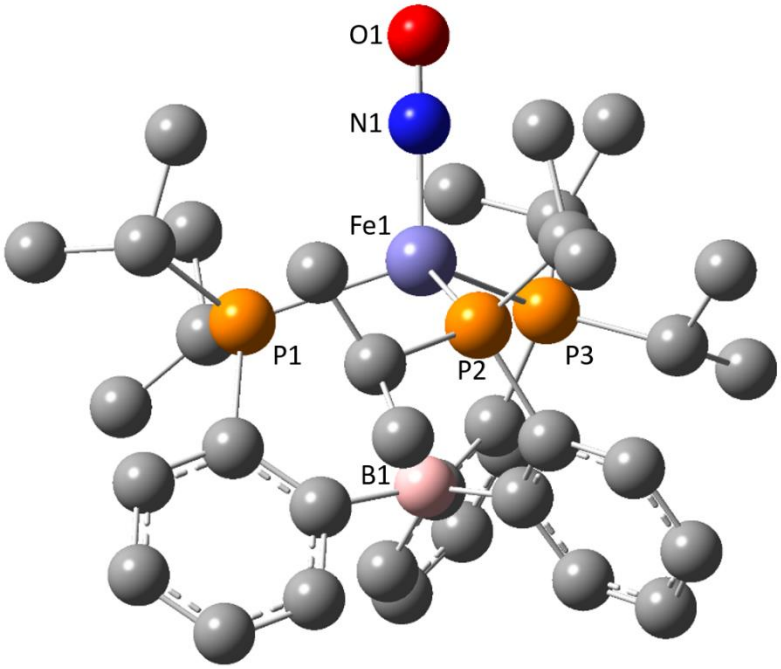


Table S11: Optimized coordinates for **{TPBFeNO}^{8}** (B3LYP, *S* = 2).

Fe	0.10623623011699	-0.11275927117069	-1.28574418534749
P	-2.34005671172318	-0.29038364701494	-0.61349963044824
P	1.68350888927663	-1.86337494454120	-0.43347671728328
P	0.88341026933238	2.22110311031309	-0.48248998058855
C	-1.57075988273788	1.39629398854957	3.07252507988077
C	-0.49258663219017	3.44425579068886	-0.10871445492701
C	1.27978707571606	0.78299129666600	1.91989663470267
C	-1.42694499808450	0.64127991078718	1.88953650368439
C	-2.87412797277528	-2.07767085629859	-0.38883911699621
H	-2.00139734111272	-2.49964962346572	0.12550701055047
C	0.04837987897645	-1.64817913110399	1.85109460104668
C	1.86892914517754	-3.34498410509178	-1.56161939230625
C	-1.17205015410406	3.93501489620246	-1.40127446177448
C	-2.55051561803469	0.52680067274831	1.02759219175925
C	2.18522209305797	3.05369573193098	-1.56558567798792
C	-2.78482210630895	1.98503632422052	3.43184767152928
N	0.19685997003151	-0.27206659545757	-3.11371685795694
C	1.71661576367199	1.88508600043097	1.13154378716983
C	-3.88151780230024	1.86259233975758	2.58288940061014
C	-0.67116904881256	-2.20134576333073	2.93116121930078
C	-3.54860029366926	0.60819180234459	-1.75471721001149
H	-3.49834926404065	1.63647046867742	-1.37270179690961
C	0.49984691967624	-3.90870629497324	-1.97488307331215
C	-3.75448216144577	1.15271293211407	1.38620751244380
C	2.84780786475873	2.60859387912882	1.53716775666646
C	0.88297295765865	-2.51825459285320	1.09318617640676
C	-0.53973341203786	-3.54324246064429	3.29878878618182
C	1.92975718605318	2.75493934715331	-3.05699961396248
C	0.98777082387052	-3.86679190430293	1.45912763946403
C	0.29756441129348	-4.37726374791984	2.56341380445889
C	-3.03998006098707	0.62948481695262	-3.20923041911910
H	-2.05438384248184	1.09346774307917	-3.29730441877404
H	-3.73810335630914	1.20519230550833	-3.82870023650760
H	-2.97477074124033	-0.37685883260550	-3.63625451962862
B	-0.03207938502562	-0.07633762926847	1.73119713102149
C	2.01120940817623	0.47036604695537	3.08581542891704
C	3.11323817658703	1.22483802711709	3.49529879599626
C	-5.02739858024004	0.16728711119921	-1.73865895460110
H	-5.61625270035777	0.89603477718813	-2.30865329180780
C	2.43066629363346	4.56490086506412	-1.37892316411389
C	-4.09399304278881	-2.32215114441705	0.51446281257726
C	2.70922046333213	-3.02616144210906	-2.81268955490345
C	3.53544111195193	2.29636053332336	2.71339642368518
C	4.15399582741388	-0.49213701508940	-0.88231838634036
C	3.41646278150074	-1.39833239461768	0.12029244003915
C	-0.15229281651526	4.60741738880224	0.83811393494675
C	-3.01510836948911	-2.79954187379775	-1.74288192728375
C	4.28139358466184	-2.59450688577624	0.55050474695498
O	0.25648172024684	-0.43765400543055	-4.28132731187332

H	-5.46461647787237	0.10191123171960	-0.73995431117702
H	-5.16266179551849	-0.80328530725825	-2.22412517716951
H	-3.93778959745917	-2.51893614142934	-2.25876137629331
H	-2.17767874468184	-2.59724709885465	-2.41768868687364
H	-3.05388391595154	-3.88252414362539	-1.57675978754537
H	-5.02540828739447	-1.98069895612964	0.05399924103943
H	-4.19443524449577	-3.39993598856918	0.69294535335007
H	-3.99132122517246	-1.83209114520053	1.48706060664564
H	-1.33589736972946	-1.56234589842579	3.50660418677228
H	-1.09827621399537	-3.93132459931383	4.14606518693407
H	0.40506479349210	-5.42524448113067	2.82892003832032
H	1.60449504240129	-4.54598187908388	0.87960616745682
H	2.30012181774828	-2.18238892074676	-3.37822080490436
H	2.70333905894205	-3.89839711697707	-3.47691200764113
H	3.75271175723252	-2.80857760074383	-2.57326668792221
H	2.40451866704358	-4.11004718968930	-0.98648552009022
H	-0.14160696660153	-4.13620665421954	-1.11794385632151
H	0.64273313830806	-4.83695385030800	-2.54056684773123
H	-0.02770100474008	-3.20588795102079	-2.62823694867007
H	4.50518376312167	-1.03948715598863	-1.76136137223635
H	3.52367242420384	0.33131833780057	-1.23311641676045
H	5.03419705803463	-0.05576087158309	-0.39567654889246
H	3.20945935477202	-0.79732220738201	1.01176036872645
H	4.55067500667747	-3.23500634290620	-0.29653881373685
H	3.78632680236066	-3.21161238448282	1.30729750195887
H	5.21696108738782	-2.22569986051053	0.98803272198900
H	1.70864036100831	-0.38356712160476	3.68712562094862
H	3.64426116020507	0.96185219197322	4.40606737919156
H	4.40140005896160	2.88491876177513	3.00341652590214
H	3.21612200209064	3.42918672762170	0.93351411917837
H	2.73879519457217	3.18792434406706	-3.65741853053643
H	1.88952037867884	1.68334547619582	-3.26586423305069
H	0.99058010985349	3.19888103573735	-3.40572367637488
H	3.10277227300306	2.52480221500819	-1.27594801182105
H	3.31124972148618	4.85299561606317	-1.96592501736626
H	1.58944029232471	5.15723863096906	-1.75162597000243
H	2.61325506127474	4.86200652275587	-0.34335041878187
H	-0.53824751816559	4.62797329722901	-1.96319380281907
H	-1.44054695416965	3.11009535070958	-2.07090522694553
H	-2.09333996512624	4.47295383682869	-1.14738099802453
H	-1.21184081164279	2.80711131425741	0.41668490223199
H	-1.08234738008477	5.10861542108469	1.13376404271480
H	0.34181582790571	4.26195232841153	1.75125902688073
H	0.48584907490022	5.35797024803342	0.36484570626195
H	-0.71249770038851	1.52211082215709	3.72780813728181
H	-2.86300122522276	2.54866006632116	4.35745131677375
H	-4.83069890261081	2.32683812517998	2.83555026734180
H	-4.61385653832662	1.10265101966231	0.72936549655903

Figure S41: The gas-phase optimized geometry of **{TPBFeNO}^{8}** (B3LYP, BS) with hydrogens omitted.

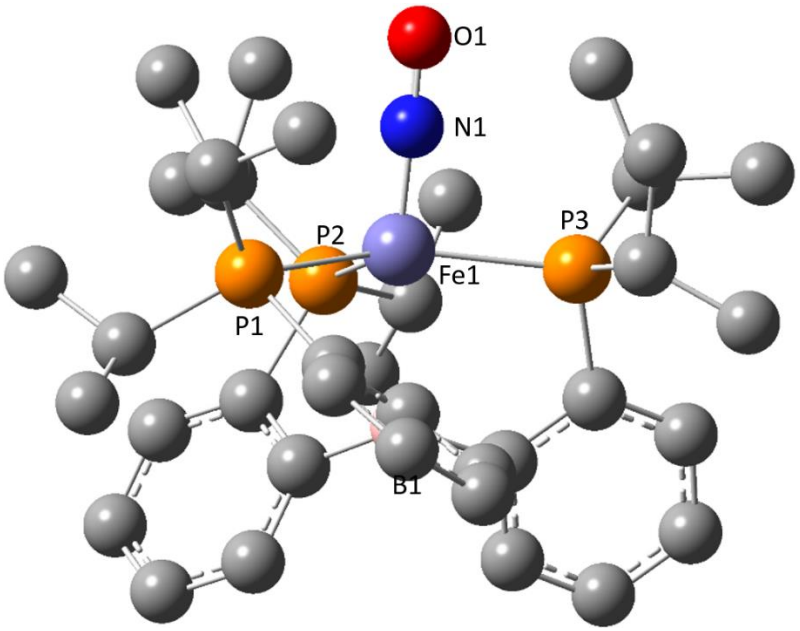


Table S12: Optimized coordinates for **{TPBFeNO}^{8}** (B3LYP, BS).

Fe	-0.09626905237270	-0.41912689323610	-0.72566062084693
P	-2.43179743899203	-0.19524433338055	-0.38726076602271
P	1.96127007638548	-1.54388657363285	-0.44077944506710
P	0.71796272841620	1.78767026864759	-0.45042852063103
C	-1.54812791592015	1.29748331144020	3.29360062639317
C	-0.51933789492593	3.19097850167173	-0.19567270433805
C	1.23035374003818	0.80878635752302	1.98857748105893
C	-1.46130931886096	0.64642893946048	2.04871209942072
C	-3.17511009741444	-1.92562845109864	-0.34007109188912
H	-2.39902337761271	-2.48070457478138	0.19801027996838
C	-0.02819745280639	-1.58668011778315	1.46807775339666
C	2.43756853924707	-2.80375317834326	-1.75130701477540
C	-1.13715417996629	3.72687113792404	-1.50129575510250
C	-2.64596716035621	0.53860629277269	1.27785490344783
C	1.89857356956540	2.28826219619499	-1.83664279836439
C	-2.75678894894026	1.79899370093407	3.77973467526371
N	-0.29877536459354	-0.90759743172661	-2.30106700964099
C	1.73167373333116	1.76160292473329	1.07813455159748
C	-3.91768623158523	1.66950138782455	3.01763634403510
C	-0.93409317737272	-2.27528084640137	2.32276625714627
C	-3.44335683019737	0.87627742397097	-1.56512530956954
H	-3.24177484368752	1.88290476050869	-1.17879731390434

C	1.34555275432659	-3.81448689907339	-2.15172133290002
C	-3.85918848181569	1.04542747846337	1.77047411386083
C	2.87972030445394	2.50503779782547	1.38608012219644
C	0.98420152221906	-2.38329784193532	0.84434939324202
C	-0.79454360852181	-3.62545481721078	2.62301029922462
C	1.41575761499040	1.89281774595234	-3.24340265411769
C	1.09948011968795	-3.75376727703774	1.13509495144621
C	0.23518973712375	-4.36868472066412	2.03586381399226
C	-2.94130487829354	0.81554211932117	-3.02032715903052
H	-1.87868453122599	1.04620497827167	-3.11357446109775
H	-3.49615127124156	1.54809763890363	-3.61868312713341
H	-3.11036015490685	-0.16754503883332	-3.47007272839771
B	-0.07923134020083	0.01543679045320	1.56679671136782
C	1.88946695447014	0.63999191421931	3.21730945679767
C	3.03234417374181	1.38352087922561	3.52574504896862
C	-4.97384336896908	0.67368836412821	-1.56697792398044
H	-5.42372475517433	1.45894262805134	-2.18639966453624
C	2.36217875891612	3.76146616742356	-1.86056402235436
C	-4.47632821912451	-2.07265991401161	0.46980443737106
C	2.96068932278352	-2.09963518244416	-3.02385386588844
C	3.53047576067413	2.31078676818086	2.60746246224355
C	4.65471718447734	-0.48035210629420	-0.54520885462799
C	3.59502959107724	-1.09132766358532	0.38867403571023
C	-0.01954505564229	4.35301642768254	0.68211137446464
C	-3.31104047461433	-2.56985527016998	-1.73284051506265
C	4.20247949643118	-2.26106745237242	1.18540228192588
O	-0.42671784776378	-1.12843430958498	-3.44021271113522
H	-5.43531156529390	0.73850024509073	-0.58071373879184
H	-5.25502812636255	-0.28578327912288	-2.00988116301175
H	-4.09508164117570	-2.09938178723242	-2.33375684416116
H	-2.37996288553449	-2.54335776416436	-2.30483489341596
H	-3.58993704091067	-3.62313753540594	-1.60903564488461
H	-5.32834784927117	-1.58983233468044	-0.01687584546885
H	-4.71512840299336	-3.13957076026658	0.55919176089944
H	-4.38457093301224	-1.66749492605412	1.48130423504808
H	-1.72520814329426	-1.71395829933995	2.80805469500885
H	-1.47730111963397	-4.09757585596812	3.32417570838402
H	0.36079417062789	-5.42056446416181	2.27741961164700
H	1.88545799347100	-4.34142883906100	0.67204976728714
H	2.15603083466687	-1.57208731553311	-3.54445826721815
H	3.35289151161376	-2.85693417041095	-3.71274414646659
H	3.76390849262606	-1.38702502416028	-2.82921454314867
H	3.27150248978613	-3.36287997776531	-1.30638376465325
H	0.92689371427614	-4.36472783065802	-1.30766640436540
H	1.78932409192674	-4.54615688411430	-2.83758705434948
H	0.52133340471732	-3.33415801370922	-2.68363322371724
H	5.12709209911725	-1.23840133080706	-1.17817678716456
H	4.25783687091641	0.30696630534322	-1.19333062236042
H	5.44522668784310	-0.03216967529081	0.06775469411939
H	3.29681262390414	-0.32377728577555	1.10436277814924
H	4.50343863908672	-3.09484790309114	0.54001045683330

H	3.52211304429013	-2.64301561887091	1.95078730255254
H	5.10757437268243	-1.90666802765896	1.69340655204681
H	1.52297838336606	-0.09491689982341	3.93134134064980
H	3.53983091689880	1.23161249193003	4.47487042059153
H	4.42472461701115	2.88321979095229	2.83813223819916
H	3.29081075998009	3.22362035927737	0.68711236202553
H	2.18462844710722	2.16584991483370	-3.97641131468787
H	1.23410768994545	0.82213512492260	-3.33882553187864
H	0.49967018697333	2.42196514018628	-3.52544206339183
H	2.77313972441849	1.66909533908918	-1.60106055301598
H	3.22776599542736	3.84341608236174	-2.52929880663942
H	1.58734601670868	4.42070435883808	-2.26045678749770
H	2.66147041406096	4.15519817860285	-0.88829036076698
H	-0.45362253325526	4.39530182879484	-2.03136626308177
H	-1.43404619757144	2.93639388110857	-2.19419190772933
H	-2.03310403924980	4.31224479430535	-1.26111122841374
H	-1.31356553657395	2.69037508567144	0.36793447557140
H	-0.85106303864971	5.04835632213962	0.85193624099472
H	0.33347869514446	4.01172739329708	1.65828255417383
H	0.78551950464370	4.91942130710134	0.20408908329517
H	-0.65061673412223	1.41328764047522	3.89499159177729
H	-2.79011549833285	2.29335368489280	4.74703328265727
H	-4.86386124987620	2.05977042597043	3.38198695532492
H	-4.77027226738167	0.96629809983467	1.19073954891927

Figure S42: The gas-phase optimized geometry of **{TPBFeNO}^{9}** (BP86, *S* = 1/2) with hydrogens omitted.

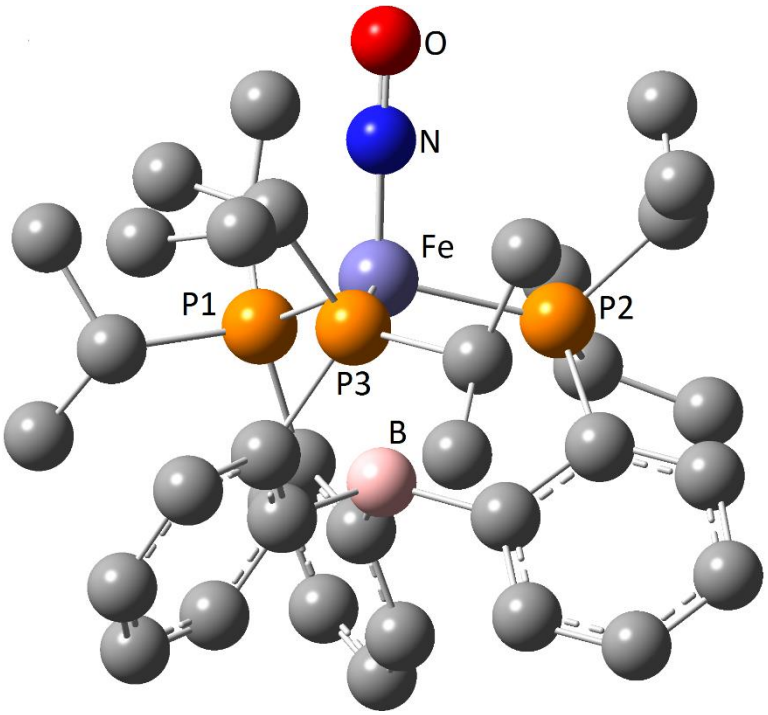


Table S13: Optimized coordinates of **{TPBFeNO}^{9}** (BP86, *S* = 1/2).

Fe	0.04522501	-0.02799095	-1.06533957
P	-2.11134537	-0.83497551	-0.57033508
P	0.21925457	2.17675036	-0.49776736
P	2.05017072	-1.03226510	-0.47926388
O	-0.21974564	0.07424373	-3.89609331
N	-0.05655682	0.02506752	-2.71688591
C	1.47142114	0.00854724	1.94410600
C	-3.56148682	0.33586874	-0.19522999
C	2.57456917	-0.45524228	1.17913400
C	3.89142295	-0.39222151	1.67978768
C	1.74855399	0.51129041	3.23837805
C	3.58784802	-0.80780786	-1.57105882
C	-1.70696200	1.27877022	2.93891947
C	-0.77881936	-1.45760068	1.70481566
C	-0.90733665	1.22936154	1.77222690
C	-2.75983051	-1.92002986	-1.97863503
C	-0.45822022	-2.23687148	2.84298642
C	1.86447237	2.90327789	0.11425121
C	1.76341495	-2.90163905	-0.27907936
C	3.05855766	0.57427135	3.74376869
C	-0.84013906	2.40980479	0.98286197
C	-1.54006860	3.57831230	1.34435390
C	-4.53121327	-0.16114636	0.89411019
C	-2.64795577	-3.01412344	1.27849273
C	-2.41683770	2.43841147	3.29988082
C	1.75175351	-3.65947873	-1.62281092
C	4.13562659	0.12904740	2.96112296
C	-1.88213073	-1.88750191	0.91380563
C	4.73273862	-1.83727108	-1.43020119
C	-4.32003407	0.78985063	-1.46029556
C	-1.19961291	-3.37881901	3.19108555
C	-1.85255460	3.22843073	-2.12622798
C	-2.30264944	-3.76624518	2.41372663
C	-0.38891093	3.47278484	-1.72580944
C	2.65659440	-3.61140262	0.75623888
C	-4.12727576	-2.62442058	-1.81597535
C	-2.33751792	3.59142669	2.50237172
C	3.22880940	-0.62772862	-3.05907724
C	1.76840130	4.32686742	0.69470494
C	-1.70934491	-2.95561963	-2.41641976
C	3.02774547	2.80854138	-0.89617071
B	-0.03362909	-0.06861546	1.34507795
C	0.48452424	3.57294221	-2.99302566
H	-0.32916281	4.43889031	-1.18542232
H	1.51045033	3.90959856	-2.78023899
H	0.54230608	2.60488560	-3.51978110
H	0.03414509	4.30311358	-3.69226793
H	-1.93794759	2.29858410	-2.71455408

H	-2.21437694	4.06055781	-2.75983259
H	-2.52104025	3.14880116	-1.25299723
H	1.55138177	5.07723922	-0.08846135
H	2.73834743	4.60524154	1.14956966
H	0.99676084	4.40775535	1.47802383
H	2.08684249	2.21375289	0.94792494
H	3.98994046	2.72462417	-0.35751899
H	3.09082296	3.71091064	-1.52959082
H	2.93467908	1.93803944	-1.56610104
H	-1.48450719	4.47917828	0.72114500
H	-2.89738689	4.49431149	2.77263563
H	-3.04113865	2.43947638	4.20197716
H	5.01946162	-2.04148758	-0.38655806
H	4.47709680	-2.80125324	-1.90022724
H	5.62906748	-1.45123114	-1.95259889
H	2.78246745	-1.54336565	-3.48536685
H	4.14363079	-0.40246102	-3.63987785
H	2.51245053	0.19444780	-3.21445049
H	3.97240147	0.16042355	-1.19745393
H	2.29283111	-4.64695995	0.89970322
H	3.70832795	-3.67394442	0.42753897
H	2.63139437	-3.10604962	1.73518895
H	1.26770430	-4.64509277	-1.48924485
H	1.19749329	-3.12122164	-2.40902335
H	2.77197617	-3.84791545	-1.99764024
H	0.73277912	-2.91087059	0.12248424
H	4.74025648	-0.72475469	1.07420708
H	5.16262630	0.19267739	3.33913126
H	3.24074513	0.98676408	4.74378953
H	0.92068355	0.89173825	3.85004826
H	-2.85630467	-1.17560965	-2.79404804
H	-4.50538710	-2.91380773	-2.81511852
H	-4.03036829	-3.55634698	-1.23305377
H	-4.89934389	-2.00276334	-1.33741189
H	-2.08047397	-3.52270005	-3.29102845
H	-0.76058976	-2.47607322	-2.70102950
H	-1.50322963	-3.68016576	-1.60775379
H	-3.03685347	1.21619513	0.21610662
H	-4.93961119	1.67317835	-1.21650052
H	-3.64391134	1.07904582	-2.28135867
H	-5.00160469	0.01076435	-1.84165964
H	-5.27213415	0.63254210	1.10858794
H	-4.00424660	-0.39445820	1.83290993
H	-5.09070925	-1.06209847	0.58527611
H	-3.51457772	-3.31540717	0.68418348
H	-2.88913520	-4.65278726	2.68137310
H	-0.91883536	-3.96553428	4.07454518
H	0.39224729	-1.93780507	3.46840461
H	-1.78879729	0.38237665	3.56761996

Figure S43: The gas-phase optimized geometry of **{TPBFeNO}^{9}** (BP86, *S* = 3/2) with hydrogens omitted.

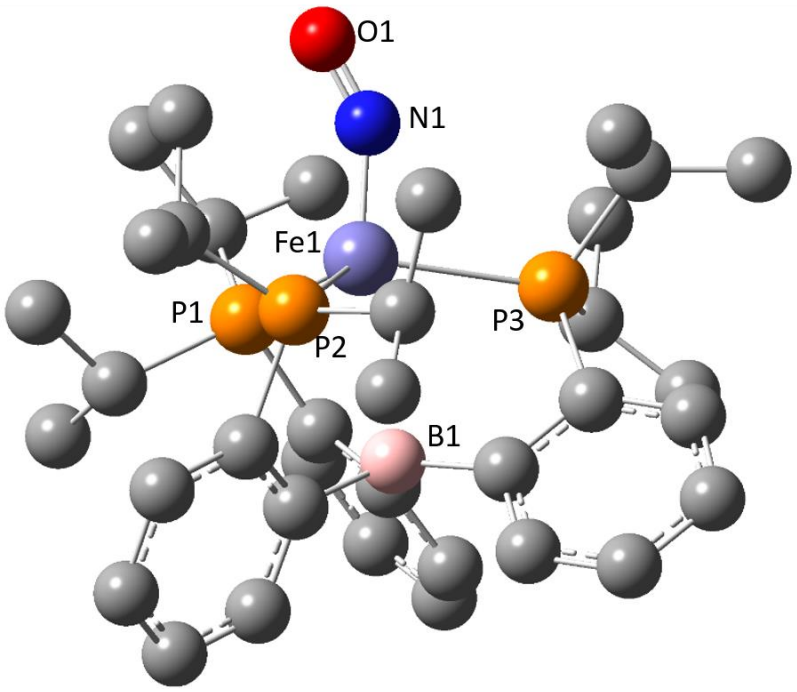


Table S14: Optimized coordinates of **{TPBFeNO}^{9}** (BP86, *S* = 3/2).

Fe	0.07287967446564	0.04584869291836	-1.10721753103155
P	-2.19520201151619	-0.91488461640577	-0.54346036761994
P	0.29694948486146	2.28639512400870	-0.52336443369485
P	2.03018882887065	-1.06937562510042	-0.47454333208027
O	0.11052734557979	0.36971255009837	-3.92070522888044
N	-0.21053880599895	0.01804303771971	-2.80854216790163
C	1.47828650914032	0.02259840648206	1.97688335968607
C	-3.62079097856318	0.26506629125131	-0.13997271791587
C	2.55145839359030	-0.48350796505506	1.19110849883457
C	3.87959364523924	-0.41375918780308	1.65899942191102
C	1.80001065119471	0.59006859288712	3.23398739418268
C	3.57883175744106	-0.84000425597766	-1.54892522598529
C	-1.80918304642015	1.29168879121500	2.84230319771361
C	-0.76721225714024	-1.47215056651883	1.74292304608323
C	-0.92157484672390	1.24066236315657	1.73709956735105
C	-2.87402688075029	-2.02993797802390	-1.90896130320254
C	-0.37502796440142	-2.30073934123999	2.82666760406111
C	1.91942376428374	2.99936916836608	0.14488321303202
C	1.72324879974483	-2.92981580810903	-0.28816260552610
C	3.12322160422536	0.65873884563321	3.69947275925479
C	-0.80403801860124	2.42152225297754	0.94423013697954
C	-1.53803811715393	3.58195243810406	1.26641156079756
C	-4.63985778967826	-0.25912401911741	0.88816448557983
C	-2.57194376873352	-3.09666939057364	1.29620990865860

C	-2.53629765665296	2.44869040679218	3.16330530535110
C	1.69930211443980	-3.66319668713094	-1.64451396544109
C	4.16801090437555	0.15703611749485	2.90932802194186
C	-1.88186230918013	-1.91359512498684	0.95686820611579
C	4.71223287415464	-1.88323586328498	-1.43249924573697
C	-4.30851037336136	0.79200538793645	-1.41590560689257
C	-1.05619332893425	-3.48336462137844	3.14882592247572
C	-1.76914841457954	3.31200007355894	-2.16364080956071
C	-2.16671694843789	-3.88129416814341	2.38659671305346
C	-0.32451717486973	3.59874113778636	-1.72180371533074
C	2.61231588625836	-3.66052600836112	0.73441452214810
C	-4.26119469225897	-2.69324162594960	-1.77002518934946
C	-2.40194101870634	3.60072003445363	2.37335454718495
C	3.21365794944094	-0.62681830138115	-3.03082677476413
C	1.81466425740905	4.43008426811086	0.70260667075444
C	-1.82375547419345	-3.08351191094308	-2.30136481419632
C	3.11495842673710	2.86972145561440	-0.82074947791918
B	-0.04425981130654	-0.07637321546312	1.48958606319621
C	0.58556333419752	3.73160993340703	-2.96096656338461
H	-0.30535248356290	4.55943558960210	-1.17098029603730
H	1.59249656955413	4.09739564124049	-2.71027750692576
H	0.68551572735530	2.76971645336477	-3.49116849752905
H	0.13702081951809	4.45584060217790	-3.66584825928475
H	-1.81506221604535	2.37554062511755	-2.74395485729910
H	-2.12917079296014	4.13078642123999	-2.81367428017865
H	-2.46022723049678	3.22477804545167	-1.31000054163538
H	1.64575895700983	5.17108029102370	-0.09941674727607
H	2.76200076838263	4.70311172536028	1.20332883048395
H	1.00503989462915	4.52815735041651	1.44409098511790
H	2.09904415220550	2.31519985162722	0.99332761655417
H	4.05877299516074	2.83704993946928	-0.24739087737870
H	3.18120098362531	3.72961661701625	-1.50821114051001
H	3.05864661840796	1.95662629024447	-1.43521092368322
H	-1.45096282616416	4.48163682937008	0.64775708191718
H	-2.96951145659643	4.50733723323243	2.60892801526255
H	-3.21144473139486	2.44965993444410	4.02658131747250
H	5.00426162299332	-2.10912520097239	-0.39550620581446
H	4.44253249426379	-2.83458874343149	-1.91807945264411
H	5.60747998357521	-1.49677738307440	-1.95460923801167
H	2.76545592958991	-1.53229594898996	-3.47350579787062
H	4.12706189232266	-0.39169075594994	-3.60845473211986
H	2.49613437409581	0.19556269773702	-3.17265195768901
H	3.97058896581505	0.11627831704390	-1.15452755449090
H	2.23603768219856	-4.69124657761834	0.87144484305771
H	3.65999599334664	-3.73319253007985	0.39811439006820
H	2.59891972338797	-3.16307688452919	1.71688638413896
H	1.19190212305286	-4.63807573320261	-1.53033614911097
H	1.16044669617719	-3.09553565778502	-2.42005350874182
H	2.71581982365485	-3.86706357913492	-2.01867773052608
H	0.69395280130938	-2.93122350441007	0.11461484197811
H	4.70781384542755	-0.78099552992239	1.04696550433452

H	5.20562591758682	0.21721997467923	3.25494393378099
H	3.33890470773709	1.11269932462791	4.67340085566881
H	0.99254151916626	1.00165090955509	3.85126164398535
H	-2.93213524382744	-1.30122848473356	-2.74171084314834
H	-4.57455978865075	-3.07978073833654	-2.75828343737308
H	-4.23665079191798	-3.55794127149478	-1.08634272483505
H	-5.04607454762636	-2.00625273296164	-1.42068489507666
H	-2.16924613500352	-3.65203858886134	-3.18437990864345
H	-0.86550723972744	-2.60621902727513	-2.55634698936255
H	-1.65046979681677	-3.80359188253503	-1.48246001132920
H	-3.09287170063382	1.11359266198938	0.32740852458993
H	-4.94194403832712	1.66055570146107	-1.15895376339876
H	-3.58124136066508	1.12281136847110	-2.17466633265279
H	-4.96397576853107	0.03683078291328	-1.88032139063550
H	-5.36313860234642	0.54268585793506	1.12788228339467
H	-4.14820095465795	-0.56336870042036	1.82553749118709
H	-5.21420902098671	-1.12241794495790	0.51130927283950
H	-3.43614929378919	-3.41557208320377	0.70848049661309
H	-2.71170626711551	-4.79905196760390	2.63231900921995
H	-0.72611370111137	-4.09109424432617	3.99907883391473
H	0.48100705327382	-1.99327327085881	3.43854222257050
H	-1.92897939335589	0.39451385083230	3.46111263312941

Figure S44: The gas-phase optimized geometry of **{TPBFeNO}^{9}** (BP86, *S* = 5/2) with hydrogens omitted.

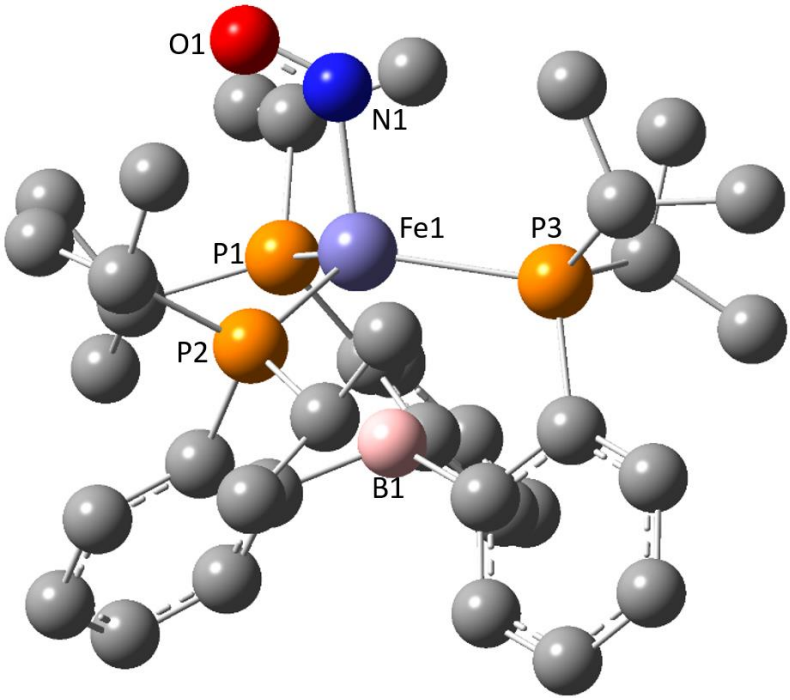


Table S15: Optimized coordinates of **{TPBFeNO}^{9}** (BP86, *S* = 5/2).

Fe	0.01534302477135	0.04922575486229	-1.03073293272680
P	-2.16852289307445	-0.91957490922512	-0.57035194015818
P	0.28490661399936	2.37120710842387	-0.51193807903683
P	2.05576321053026	-1.12872443302368	-0.45585425473293
O	-0.94820522195664	0.44854033434569	-3.70851823333426
N	-0.11480401787178	-0.14893884838329	-3.00639554518395
C	1.47578591209147	-0.00680034428383	1.94384164458018
C	-3.60139815911998	0.27652307285978	-0.25965075158600
C	2.57257298413377	-0.49961691736958	1.18664698723346
C	3.89186541853155	-0.41075667548797	1.67577254603150
C	1.76305755974159	0.56087258888594	3.20906001948603
C	3.56865954894100	-0.87533208044322	-1.57116415964247
C	-1.78723115531261	1.21172851161906	2.80843209301571
C	-0.78979777867528	-1.48785644763228	1.72511476453183
C	-0.90387187783872	1.20860250346743	1.69723354265198
C	-2.76741023419376	-2.04555436692141	-1.95696335242457
C	-0.45086029494215	-2.27825375999963	2.85117580736421
C	1.95377374982625	3.00837904684356	0.10114302676654
C	1.78897955903637	-2.98878863152153	-0.23527515369795
C	3.07621482384288	0.65064915823057	3.69890931426615
C	-0.76414319211121	2.44141009788607	0.98820159722101
C	-1.45535200396627	3.60043862421585	1.39946948647740
C	-4.65532066997004	-0.20598348241324	0.75332726717978
C	-2.68181101267938	-3.02675633356563	1.33949138293120
C	-2.47366920351549	2.36568487274584	3.21742652817875
C	1.77763282399720	-3.74677911452289	-1.57847024013741
C	4.14582043885645	0.16836148076979	2.92927855214612
C	-1.91624707318209	-1.90771283823193	0.95299588859329
C	4.75535063469521	-1.85463839031901	-1.43284861397055
C	-4.24112032039061	0.75353016401741	-1.57972324546861
C	-1.19535571150796	-3.41113807469437	3.21656710002597
C	-1.85741796203151	3.49128656520316	-1.98446265922014
C	-2.32228401348830	-3.78232813933998	2.46722359594465
C	-0.36685585926389	3.70576441822595	-1.66532358807813
C	2.70874283337393	-3.67455868142459	0.79119496459582
C	-4.13924941685227	-2.74125582543181	-1.82856630481622
C	-2.30651594212461	3.56921991653197	2.51462378709291
C	3.17072660580451	-0.74343998022742	-3.05579576525184
C	1.90459076761818	4.40696386854535	0.74122391343028
C	-1.68217904719675	-3.07571656449277	-2.31245325406407
C	3.08797175963078	2.91521830499555	-0.93995058130920
B	-0.02967406458224	-0.11584172280597	1.38725214338270
C	0.43210902493610	3.74600062078131	-2.98568964464401
H	-0.24143578368934	4.67298967400422	-1.13976608276563
H	1.49255542521003	4.00112177698404	-2.84039459142893
H	0.37038328997217	2.77565071463556	-3.50728783850002
H	-0.00570183289844	4.51222179754244	-3.65148290171517
H	-1.98773863169889	2.56553589565201	-2.56886726369607
H	-2.22636078121793	4.33147980508927	-2.60116386098355

H	-2.48464190924152	3.43093486303437	-1.08069664088325
H	1.70044983340529	5.19334099874224	-0.00741013583367
H	2.88442334139279	4.63799974544852	1.19839777787123
H	1.14175027588716	4.47301849563946	1.53397672823405
H	2.16656707043229	2.27353095989317	0.89835045956588
H	4.06451155948050	2.88628971980723	-0.42390223901396
H	3.10011664545837	3.79174601408917	-1.60933706351534
H	3.00837880854251	2.01476514803171	-1.57074416491853
H	-1.34200710273817	4.53666466492412	0.84177627871765
H	-2.84008315401069	4.47450201633717	2.82316597066803
H	-3.14106163453131	2.32505804837834	4.08588226169081
H	5.08209024258703	-2.01653281439328	-0.39411903594587
H	4.52003250215370	-2.84009705187112	-1.86607450668981
H	5.61839285603417	-1.45238950494452	-1.99575342713734
H	2.84656454914410	-1.71239231417466	-3.47197665022030
H	4.04305705092186	-0.40400782085536	-3.64469685717358
H	2.34009711246335	-0.03487268097665	-3.20722961114893
H	3.91480398925386	0.11682790513029	-1.22309047611392
H	2.37166883702429	-4.71708673247061	0.94134274384793
H	3.75644341846456	-3.71171667999206	0.44865785420471
H	2.68372453800849	-3.16664764569476	1.76812183351198
H	1.30804661294286	-4.73734068126039	-1.43974704080289
H	1.21251620882760	-3.21587183095041	-2.36054937726282
H	2.79833834862928	-3.92023784935786	-1.95668940575212
H	0.76320907866294	-3.00939017337540	0.17687674492888
H	4.73579925085748	-0.76871128653087	1.08000979702237
H	5.17516030588206	0.24809020525578	3.29511097031533
H	3.26613056027642	1.10841542364719	4.67648554977807
H	0.93826600418665	0.96100918352247	3.81062113260963
H	-2.82126740862966	-1.32415575702554	-2.79468381324256
H	-4.43546842915012	-3.12929092829744	-2.82100369785646
H	-4.09383073676401	-3.60878892294299	-1.14954848658869
H	-4.94389270809547	-2.07560660025568	-1.48159721840555
H	-2.00882324098170	-3.67970491554607	-3.17887683506340
H	-0.74581175420069	-2.56633366001120	-2.58802229018929
H	-1.48820975354595	-3.76691667888481	-1.47310901522917
H	-3.08324294558285	1.13856600694361	0.19569157614464
H	-4.85353141195898	1.65274754665642	-1.38662309126787
H	-3.48779246575499	1.01527221988382	-2.34082406325777
H	-4.90762670865198	-0.00975575484478	-2.01467850061924
H	-5.38106066293801	0.60771829253967	0.93804371906866
H	-4.19748535340888	-0.47710296905755	1.71764334066431
H	-5.22247452268101	-1.07912079002733	0.38812675432979
H	-3.56168088728068	-3.32093662490869	0.76204856203500
H	-2.91437119402917	-4.65958857468332	2.74896004385209
H	-0.90108974278782	-4.00005556630867	4.09296250960013
H	0.41362608635651	-1.98629926844407	3.45906578521373
H	-1.93041344450023	0.27999551457853	3.36785964570347

Figure S45: The gas-phase optimized geometry of **{TPBFeNO}^{9}** (B3LYP, *S* = 1/2) with hydrogens omitted.

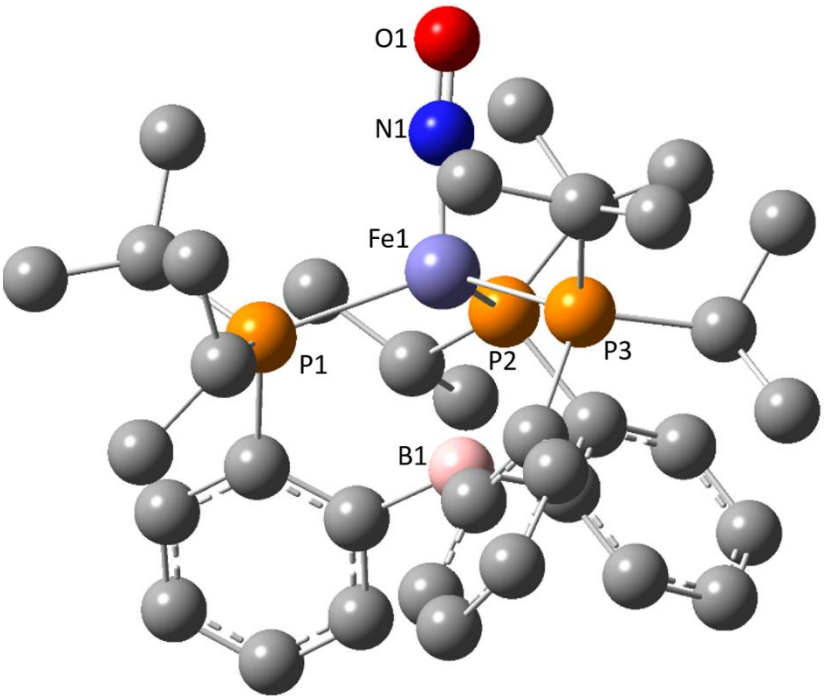


Table S16: Optimized coordinates of **{TPBFeNO}^{9}** (B3LYP, *S* = 1/2).

Fe	0.03806671608343	0.01133392384564	-1.13653321678151
P	-2.20577339010285	-0.88864280202808	-0.57950148449994
P	0.25833793692965	2.32350975665819	-0.48443647941551
P	2.09823435059367	-1.12907858011594	-0.49332560432074
O	-0.20623922265969	0.14082993821939	-4.05438489137114
N	-0.05856360071720	0.08167425724370	-2.87539914086906
C	1.47207255226222	0.00870560617157	1.90494481670305
C	-3.64456014271313	0.27513648632557	-0.20270664257388
C	2.56351278217046	-0.49950180393205	1.16113521047059
C	3.87085773446840	-0.43903244181797	1.66857475908542
C	1.75963854135851	0.55761614805877	3.17116919946639
C	3.64264871897340	-0.89981894580680	-1.56177652858397
C	-1.73760734914283	1.27788579938058	2.88613807712572
C	-0.80287539138747	-1.44708155543440	1.69159712686762
C	-0.90718326174776	1.25550289735992	1.74772949606797
C	-2.83570859040978	-2.00381248141103	-1.95976180777141
C	-0.45788255969508	-2.22127809775642	2.81824569257805
C	1.89383816922014	3.03534331840572	0.13566420897069
C	1.81634369346600	-2.98176945569253	-0.26299840550674
C	3.05999174262930	0.61516353858644	3.67793869287891
C	-0.80296005370287	2.45755439170768	1.00444082933214

C	-1.49614041711104	3.61189631466653	1.39726645564847
C	-4.65746292545009	-0.22777452823732	0.83930019118175
C	-2.65165801909458	-3.01686625537747	1.30958864721176
C	-2.43347640084399	2.42632053476255	3.27465222065125
C	1.75745064488364	-3.74344426137738	-1.60034745883679
C	4.12354895101551	0.11986083870153	2.92245669847347
C	-1.91213259904847	-1.88807032700514	0.92384405598009
C	4.79388659943726	-1.91692412590161	-1.42121492709977
C	-4.34966669186146	0.77014792075711	-1.47942471227884
C	-1.17744616673359	-3.36118209494694	3.18441076760451
C	-1.85359364639696	3.34457260287920	-2.06644454691933
C	-2.28507201428400	-3.75840269627910	2.43430541369728
C	-0.39761124850170	3.62708996694397	-1.66779988010958
C	2.72955804943439	-3.69892923566475	0.74470946168138
C	-4.18928623080048	-2.72628076030141	-1.80493834489691
C	-2.31501329895441	3.60008010169878	2.52919517983729
C	3.28648559443346	-0.72846927738578	-3.05014853372910
C	1.82486938054685	4.47538641951210	0.66812073034475
C	-1.75948362587016	-3.01440193830613	-2.38507293663180
C	3.06748475355607	2.87646963163600	-0.84872613241142
B	-0.04887158994228	-0.05952917645753	1.36389437169455
C	0.46417000366284	3.75880883678048	-2.93710002198700
H	-0.36558085563495	4.58536337520969	-1.13248034274386
H	1.47235067618140	4.12331194130413	-2.72713711954924
H	0.54810928806847	2.80207253761017	-3.46407436417849
H	-0.00605199096759	4.47393465437428	-3.62459695499929
H	-1.91774596919308	2.42589700017123	-2.65869705891520
H	-2.23432174011238	4.16666534772594	-2.68661076613471
H	-2.51367892968378	3.24327173193876	-1.20023423099948
H	1.63838744070649	5.19987751316239	-0.13427184588576
H	2.78528789324662	4.74367522255337	1.12799894878744
H	1.04877786117167	4.59720317387096	1.42960058839189
H	2.09254600592457	2.37585792521409	0.98714548104826
H	4.01699323771671	2.89513745783099	-0.29885733804971
H	3.10251890386012	3.69180680442709	-1.57865283309669
H	3.01802423640109	1.93642506343046	-1.40495706483675
H	-1.41730929062785	4.52646316686433	0.81494341844051
H	-2.85899039982905	4.49624665241951	2.81769369364104
H	-3.07175875857913	2.40212704066468	4.15548821635884
H	5.09344868200883	-2.10168541289282	-0.38699089014306
H	4.54009692486381	-2.88172829276888	-1.86997707139054
H	5.67356798743263	-1.53584059103458	-1.95675513398864
H	2.85596519534754	-1.64358814815989	-3.47206952210322
H	4.19415265250981	-0.49702900960362	-3.62301301700696
H	2.56668984422877	0.07768579974419	-3.21009174380946
H	4.01719566915918	0.06563999859296	-1.19916340606038
H	2.35446840785970	-4.71764841247770	0.91070031103272
H	3.75929057550607	-3.78511787270488	0.38334326609669
H	2.74909170550186	-3.18885760176062	1.71175335145124
H	1.29704296324874	-4.72733526728818	-1.44412313040525
H	1.16696866276917	-3.21862361356466	-2.35651004380031

H	2.75501356292473	-3.91670560989073	-2.01571364446258
H	0.80650705608845	-2.98889531291396	0.16396141784456
H	4.70814698537551	-0.80889284035710	1.08667723247322
H	5.14227349912534	0.17243279865642	3.29888783864914
H	3.24308773153059	1.05679446469770	4.65526961715532
H	0.94615003017436	0.96921795752608	3.76426062222614
H	-2.94098363040297	-1.27904557292776	-2.77881216674004
H	-4.51689975364270	-3.08323345715772	-2.79039872517257
H	-4.10544443827664	-3.60856321717555	-1.16279806150834
H	-4.98301305389309	-2.09081081237604	-1.40646951643989
H	-2.11039236173060	-3.59069065191842	-3.25077235556664
H	-0.83201532955810	-2.51364174278167	-2.67152604778989
H	-1.53703287231816	-3.72474775783950	-1.58002907232497
H	-3.13122286363382	1.13298102175569	0.24299755236836
H	-4.98249970534751	1.63258181088033	-1.23464659571722
H	-3.64270356310327	1.09005782427359	-2.25040544588210
H	-4.99966295606934	0.00492310874437	-1.91572449765511
H	-5.38063330593174	0.57047530843623	1.05292754007492
H	-4.16990976326509	-0.49722298906639	1.77976472264868
H	-5.22349364565621	-1.09857934258702	0.49071815942581
H	-3.51747827035091	-3.32857218756723	0.73700988585856
H	-2.85616007850936	-4.64031601737689	2.71397137135617
H	-0.87640830600131	-3.93501442943095	4.05844481931930
H	0.39314887952278	-1.91915110160655	3.42386987304172
H	-1.84806943408970	0.37061318408411	3.47656098270719

Figure S46: The gas-phase optimized geometry of **{TPBFeNO}^{9}** (B3LYP, *S* = 3/2) with hydrogens omitted.

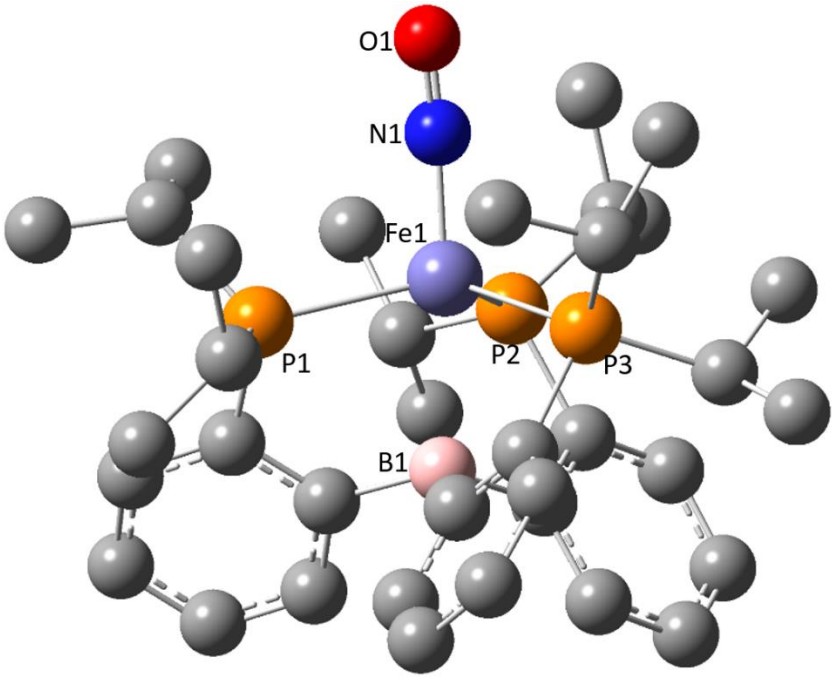


Table S17: Optimized coordinates of **{TPBFeNO}^{9}** (B3LYP, *S* = 3/2).

Fe	0.00326410162038	0.05057430716326	-1.04055380726185
P	-2.19782151284015	-0.95114411830408	-0.60772802402332
P	0.26699713247096	2.47689363590442	-0.43256340886062
P	2.08275259679672	-1.22922605861836	-0.53119958054165
O	-0.31147046101592	0.27101723953257	-4.04018191881319
N	-0.12047605582157	0.17235192289040	-2.86014379019318
C	1.46566254906567	0.03179362414893	1.83406865161740
C	-3.62292051646604	0.23110816869631	-0.25699779313503
C	2.54540009385119	-0.50840103252259	1.08854634065115
C	3.86349405451735	-0.42415357165362	1.56719196994355
C	1.78619132331382	0.63249021733147	3.07063028591664
C	3.60903242333698	-1.04389508878342	-1.62980257895924
C	-1.78420459045523	1.26216118542948	2.86480041586827
C	-0.81536407040024	-1.43298347795940	1.69348216750223
C	-0.92514079909454	1.27634713783565	1.74520760293995
C	-2.80606458502010	-2.06026739101611	-1.99587610193142
C	-0.47366090717909	-2.18258839718456	2.83819476120097
C	1.90445897254635	3.15720854967382	0.20380008916617
C	1.79112362678877	-3.06387065063463	-0.21185856689726
C	3.09541972133847	0.70827997833262	3.54895417117003
C	-0.80314751532841	2.51429266963597	1.05510653921869
C	-1.50069797186269	3.65402239321459	1.48554059212031
C	-4.66196780347243	-0.26632506999357	0.76153824366241
C	-2.61376529066275	-3.06394329263898	1.29953208301924
C	-2.48012019654089	2.39640094522254	3.28998451326675
C	1.72668249512768	-3.89114856665743	-1.50922609716888
C	4.14368725767075	0.18325119341335	2.79125887285993
C	-1.89891302190022	-1.91921535959619	0.91280924409556
C	4.77503671261599	-2.03894200031130	-1.45809958850069
C	-4.29174339294964	0.73581837581073	-1.54908167322545
C	-1.16740254632598	-3.33736178175751	3.20700801197456
C	-1.85688095493252	3.46902994581545	-1.99274670613125
C	-2.24841925709052	-3.77827201587566	2.44167895377462
C	-0.41368357495029	3.79551534616474	-1.57741430785183
C	2.71559345518135	-3.72581506545527	0.82307372615209
C	-4.14495997452290	-2.80828792898424	-1.84482754253551
C	-2.33986332994251	3.60158308256494	2.59994164785412
C	3.21552615912041	-0.95979443938474	-3.11712189994866
C	1.85588257072187	4.61822636860799	0.67726933225355
C	-1.70327134920172	-3.03434537787338	-2.43682558192463
C	3.08821596271105	2.92060214105121	-0.75099895989117
B	-0.07267824621877	-0.04240320858589	1.33758695707736
C	0.45797877085380	3.96626431195997	-2.83525595795006
H	-0.41485409310658	4.74514404861016	-1.02596065308391
H	1.45446649698119	4.35379428179726	-2.60722326083994
H	0.56950968208487	3.01741690766252	-3.37210486632353

H	-0.02176638527251	4.67920844784479	-3.51823382942832
H	-1.88347721252123	2.55507843590185	-2.59543018753962
H	-2.25917179531833	4.28473830300924	-2.60747793747097
H	-2.52055555457240	3.33774196344568	-1.13286702652377
H	1.71235633297780	5.31469009408638	-0.15768237073137
H	2.80639724867475	4.88168871494050	1.15965459586987
H	1.05753807619453	4.78615375993781	1.40716797868554
H	2.06712049331395	2.52545567246739	1.08367946725683
H	4.03199905067166	3.04891709825084	-0.20595808683651
H	3.09548575051736	3.62811416166075	-1.58624385024696
H	3.07806474173397	1.91102107449752	-1.17164444753741
H	-1.40772066357036	4.59123397273199	0.94246413433854
H	-2.88201062468421	4.48897943066904	2.91741388701458
H	-3.13351608506277	2.33809647958241	4.15813572254750
H	5.09968440654521	-2.16255764149129	-0.42213571900811
H	4.52057841753633	-3.02993393910585	-1.84559099455765
H	5.63838565149696	-1.68141151596111	-2.03474313740333
H	2.80848529876298	-1.90981068029662	-3.48143963969053
H	4.10261000122130	-0.72892217674017	-3.72146410050815
H	2.46422517473152	-0.18821853820682	-3.30081782818102
H	3.97661002032855	-0.05347335654673	-1.33011454548878
H	2.34959168147683	-4.73856552301709	1.03795244345383
H	3.74381674212603	-3.81958655888544	0.45874981868160
H	2.73645154525642	-3.17100036374663	1.76502046845533
H	1.28040360698306	-4.87103801395396	-1.29696290556931
H	1.12122391371396	-3.41230048602052	-2.28328814917686
H	2.72183291967148	-4.07376817222160	-1.92633399849294
H	0.78445221681212	-3.04843135165360	0.22190797173209
H	4.68854785255289	-0.81705963681115	0.98322592100135
H	5.17011898721528	0.24830561034757	3.14397291071942
H	3.29800672254439	1.18506728564359	4.50578859039195
H	0.98513085640909	1.06708677295420	3.66426436986408
H	-2.92659424714788	-1.32600824390387	-2.80390627724763
H	-4.45731619079189	-3.18123584144091	-2.82922881428461
H	-4.05083893714744	-3.68157961260883	-1.19188764237324
H	-4.95326918529548	-2.18173570537726	-1.46040996716364
H	-2.03932143355170	-3.60674181399048	-3.31085790107698
H	-0.79408703956353	-2.49632937363218	-2.71707654780921
H	-1.45949655466159	-3.75063173163000	-1.64331637101407
H	-3.10924699353883	1.08133027956778	0.20353260333737
H	-4.93209764301701	1.59572986403321	-1.31578480279480
H	-3.56213309616886	1.06144980332806	-2.29683904112490
H	-4.92813824757732	-0.02753719759670	-2.00885561064885
H	-5.37823507616528	0.53962173079072	0.96846056625113
H	-4.19547667711929	-0.55064403320899	1.70837244606349
H	-5.23231874675233	-1.12635180135746	0.39388784731712
H	-3.45822252778529	-3.40885377570830	0.71373579208511
H	-2.79910346602470	-4.67226700563799	2.72374355178983
H	-0.86800564418159	-3.88952457884507	4.09554614788212
H	0.35735676342944	-1.84843247398229	3.45524532996972
H	-1.91066881681991	0.33283911320817	3.41596616790788

Figure S47: The gas-phase optimized geometry of **{TPBFeNO}^{9}** (B3LYP, *S* = 5/2) with hydrogens omitted.

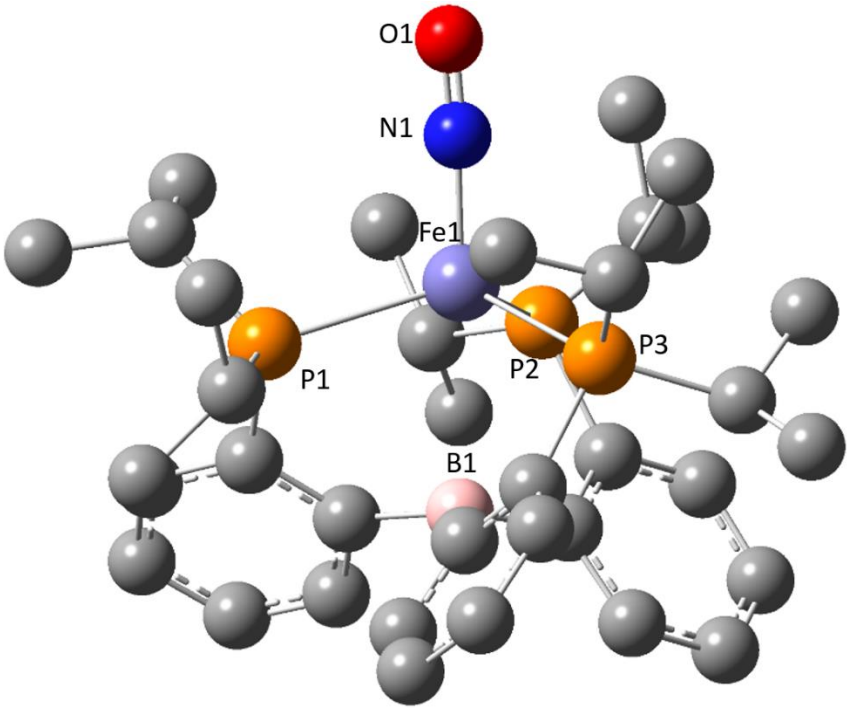


Table S18: Optimized coordinates of **{TPBFeNO}^{9}** (B3LYP, *S* = 5/2).

Fe	0.01339954037881	0.02744994675686	-1.22013742934905
P	-2.26969184415233	-0.95017994284511	-0.60014966156296
P	0.27067410922751	2.49995212028683	-0.42406313012968
P	2.12989104235079	-1.24838566622976	-0.48304222968081
O	-0.17050760564449	0.18385781657908	-4.23269900083553
N	-0.06145538098951	0.15005446509759	-3.04395239892840
C	1.47645466473905	0.09232578309773	1.90032194105136
C	-3.66283713581096	0.25612157495554	-0.22314476445050
C	2.53189063915859	-0.51370783704701	1.14869192626076
C	3.86365950908610	-0.40762275087882	1.59355097208364
C	1.85887825383823	0.81685997325996	3.05641105913518
C	3.70931485244036	-1.08505025470585	-1.51321364991084
C	-1.92423231760087	1.27285690433732	2.81817907365613
C	-0.75806238476097	-1.44441645618944	1.69436247985292
C	-0.95925088389307	1.27689470598696	1.78136864412423
C	-2.94664643554967	-2.09212229671708	-1.93637160482811
C	-0.31252109104844	-2.33025218355587	2.70977009507314
C	1.92605163894571	3.15691249484496	0.18615478376009
C	1.78146135848819	-3.07619326268885	-0.20816753823898
C	3.17921497808028	0.91249518109966	3.48793928192986
C	-0.79376346253785	2.50913390157387	1.07064157912624

C	-1.52855499626347	3.64794230528876	1.44701079086099
C	-4.69686381744880	-0.23432902502295	0.80380485446512
C	-2.52763490384713	-3.09738572052024	1.22986034399299
C	-2.65195061464478	2.40546988714202	3.17772690865621
C	1.70058787645822	-3.86287407891856	-1.52930590028060
C	4.19294692166662	0.28806857764422	2.75466944402328
C	-1.87838830277682	-1.88910915643374	0.91315123694261
C	4.83288343368656	-2.12660061848256	-1.33808784968317
C	-4.33502456339865	0.78138187505692	-1.50503338939686
C	-0.94840010578073	-3.53404700639953	2.99590800259175
C	-1.85776475762376	3.50680064052257	-1.96928249654741
C	-2.07966063137418	-3.91606083728352	2.26399202351461
C	-0.42089707696291	3.84298189390035	-1.53847552840475
C	2.67571027824744	-3.78829357087655	0.81959695868876
C	-4.31268046460590	-2.78715409271435	-1.77369955015730
C	-2.44607174700282	3.60896186006550	2.49635064759322
C	3.36431818732948	-0.94302189739404	-3.00902399575136
C	1.89589561645362	4.61689380891666	0.66440301979217
C	-1.87609505101180	-3.11025561478346	-2.36142877439500
C	3.09223532926260	2.90636595315853	-0.78641217369421
B	-0.07337618373318	-0.02784883312764	1.58647348848711
C	0.45676182428172	4.04514147689511	-2.78794169957512
H	-0.43484468669998	4.78485190238615	-0.97489997252204
H	1.43938831384247	4.45962418039998	-2.54770228572505
H	0.60225876873498	3.10404220193070	-3.33093981171078
H	-0.03643200901546	4.74852307446037	-3.47116362170584
H	-1.87191344756733	2.59969975370944	-2.58386632310559
H	-2.26440013586203	4.32522851196144	-2.57747829148825
H	-2.52657876308690	3.35716674185615	-1.11685249172687
H	1.74928240934759	5.31882165676108	-0.16538887260493
H	2.85336010706093	4.86997056690869	1.13845450912510
H	1.10597583292303	4.78784172464526	1.40314027474994
H	2.09641716817149	2.52385446054263	1.06250463856163
H	4.04496341930538	3.04983995470498	-0.26089157760591
H	3.08255388350090	3.59385581382214	-1.63806720335730
H	3.07921221028760	1.88662414542928	-1.18300447193132
H	-1.39941128144578	4.58241501858472	0.90748935272386
H	-2.99920567885739	4.50400076249831	2.77020586271230
H	-3.36973824224215	2.35419415588904	3.99367576148961
H	5.12648052224325	-2.28579580119544	-0.29746595480156
H	4.55136311779931	-3.09832100145554	-1.75489218283108
H	5.72325348359903	-1.78877032297933	-1.88488099532013
H	2.91601375945565	-1.85847948328720	-3.41120280093884
H	4.27895211294876	-0.74451123149334	-3.58297963794878
H	2.66237389183470	-0.12533899349278	-3.19291662012092
H	4.09964154985242	-0.11679795524329	-1.17413932544916
H	2.26301308015561	-4.78372130654165	1.02995637434890
H	3.69802909883909	-3.92737766370784	0.45411306091546
H	2.72183225288584	-3.23939577823454	1.76452823040075
H	1.24100353262039	-4.84223896717383	-1.34539916731444
H	1.09678911873745	-3.35058407724806	-2.28449233684573

H	2.69022868974750	-4.04582916278965	-1.95973062600762
H	0.77295286739340	-3.04071203584375	0.21814909384525
H	4.66788879000549	-0.86043929695293	1.02483026309096
H	5.22980586742525	0.34860651343679	3.07606325878143
H	3.41788712156280	1.46549730482557	4.39390605712805
H	1.07989550262274	1.30614641861418	3.63662089513281
H	-3.04859726437202	-1.37404945088454	-2.76217465354422
H	-4.62797777688808	-3.18097176763641	-2.74926756281979
H	-4.26416041076118	-3.64065016610164	-1.09068203668810
H	-5.09979753634356	-2.11631628739611	-1.42210411695902
H	-2.23068808666344	-3.68755122946756	-3.22481349727606
H	-0.94796895527082	-2.61079657739628	-2.65493066854466
H	-1.65065162816994	-3.81777471334199	-1.55534547093840
H	-3.12897827844709	1.09283450670276	0.23842471885134
H	-4.96202811135879	1.64803530232111	-1.26065252981226
H	-3.60576203698506	1.10340332367933	-2.25543917453192
H	-4.98484822573959	0.03101278483206	-1.96754010798135
H	-5.38807370690019	0.58468335424327	1.04241484155209
H	-4.21846242810802	-0.55113180008717	1.73446955933418
H	-5.29566128312979	-1.07179253322518	0.42987478410849
H	-3.39603857876154	-3.40978607166608	0.66185161763371
H	-2.60076798048940	-4.84306691344952	2.48963057771768
H	-0.57867783979818	-4.16576768822679	3.80083895367982
H	0.54512900552919	-2.03364600833894	3.30899426755254
H	-2.08360963112534	0.34862911605986	3.36917015686035

Figure S48: The gas-phase optimized geometry of **{TPBFeNO}^{9}** (B3LYP, BS) with hydrogens omitted.

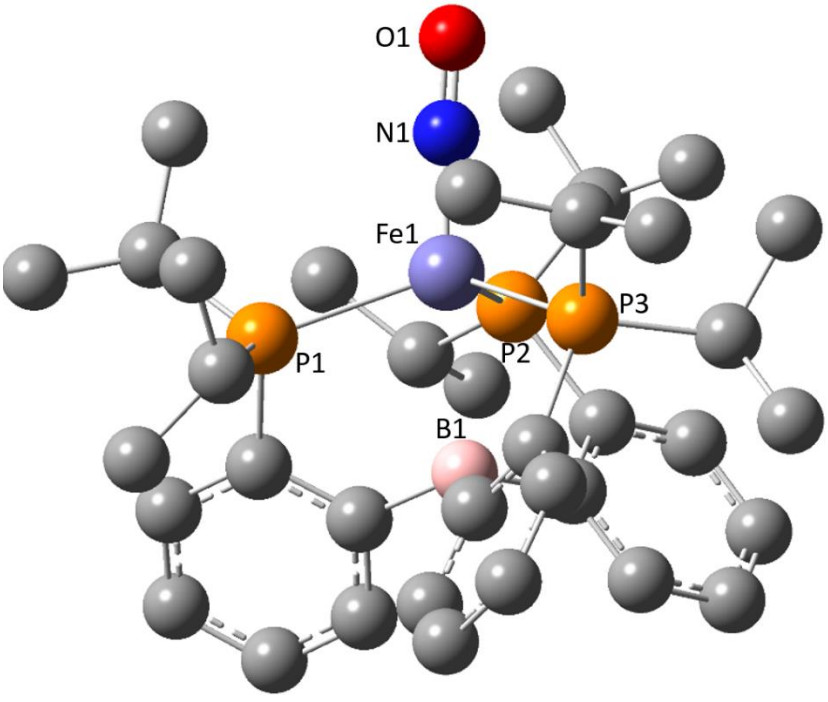


Table S19: Optimized coordinates of **{TPBFeNO}^{9}** (B3LYP, BS).

Fe	0.03813916274147	0.01252629983205	-1.13600633790127
P	-2.20272926278702	-0.88679567152813	-0.58153600962350
P	0.25404637396222	2.32340186231551	-0.48480732376773
P	2.09870592606641	-1.13026702333194	-0.49156505887440
O	-0.20606044984762	0.13591483762924	-4.05540991524842
N	-0.05815185748350	0.08162221982877	-2.87620216508551
C	1.47160941187998	0.01059702225790	1.90574242995555
C	-3.64250981355972	0.27622016603709	-0.20426364859679
C	2.56307024935568	-0.49892419670463	1.16260527739287
C	3.87023154626219	-0.43908581116003	1.67046248827698
C	1.75929924636757	0.56062219801657	3.17144662112894
C	3.64342597917757	-0.90195737068777	-1.55987199699633
C	-1.73713616398371	1.27962719951288	2.88864932685585
C	-0.80290141850933	-1.44556973502330	1.69141352695703
C	-0.90781362055223	1.25712630469826	1.74953199561740
C	-2.83295168353023	-2.00157018055327	-1.96220744897008
C	-0.45899006646284	-2.21968810014115	2.81850153228728
C	1.89177295031291	3.03339904796571	0.13167470157919
C	1.81699941791911	-2.98280301471492	-0.25928314577528
C	3.05952080559537	0.61763258777455	3.67860863833849
C	-0.80450413407430	2.45903061334322	1.00576864632321
C	-1.49666060344154	3.61366881007750	1.39922829283595
C	-4.65353597579943	-0.22646372854100	0.83966517357342
C	-2.64925952913829	-3.01717892495124	1.30559232465260
C	-2.43235713883736	2.42831075277508	3.27772359161560
C	1.75787966719788	-3.74604682321224	-1.59577654599409
C	4.12291592601348	0.12064868417694	2.92397086227769
C	-1.91033510574965	-1.88742822242841	0.92154264561279
C	4.79476646080080	-1.91862702859331	-1.41804719284201
C	-4.34974450760261	0.76884903160619	-1.48080754017844
C	-1.17805523502304	-3.36050955845476	3.18315850981924
C	-1.85880795369421	3.34524119246700	-2.06499597310335
C	-2.28381926286822	-3.75870615024921	2.43088610019601
C	-0.40248654913579	3.62751986643564	-1.66713756257150
C	2.73104862439419	-3.69837753406215	0.74883866192095
C	-4.18567703075461	-2.72556366343623	-1.80689828067560
C	-2.31415146134578	3.60211212712096	2.53223859116657
C	3.28690106241284	-0.73282446503426	-3.04845432923317
C	1.82554733189378	4.47362464981156	0.66389973033616
C	-1.75622010558562	-3.01104940841766	-2.38917213840440
C	3.06310920311550	2.87259734773713	-0.85529655371457
B	-0.04937557140127	-0.05760312327584	1.36448630037911
C	0.45883608308860	3.76011796035432	-2.93677498945007
H	-0.37012585216872	4.58542200677402	-1.13093105426251
H	1.46713236051894	4.12473940902386	-2.72688622838034
H	0.54283828728724	2.80350175234332	-3.46428402025523
H	-0.01176181755874	4.47554128377108	-3.62376039466652

H	-1.92320288419513	2.42729449526467	-2.65858325323919
H	-2.24037479017302	4.16817943142344	-2.68355261700161
H	-2.51817516046157	3.24239384262017	-1.19827990218779
H	1.63844474608755	5.19807121178792	-0.13840745019907
H	2.78706582596092	4.74113202635215	1.12198526655717
H	1.05089786821785	4.59644443476444	1.42674221355058
H	2.09109362147864	2.37394051577559	0.98298357809225
H	4.01362254977933	2.88301743375268	-0.30705472057154
H	3.10149057141901	3.69154368784847	-1.58101663377648
H	3.00748389240724	1.93581554257848	-1.41659255925255
H	-1.41825465315950	4.52816319471102	0.81660945931185
H	-2.85745217999107	4.49845551866111	2.82144024810771
H	-3.06997414520729	2.40428139032646	4.15908261609876
H	5.09434814549141	-2.10231086435796	-0.38365213430295
H	4.54113736334094	-2.88396811953491	-1.86581891445375
H	5.67441572239072	-1.53796791668105	-1.95397737877390
H	2.85550209515115	-1.64829072937440	-3.46869688943665
H	4.19452777424276	-0.50308816544992	-3.62208421998910
H	2.56768680584253	0.07363260968681	-3.20945496483422
H	4.01733683595976	0.06420751001392	-1.19847668460876
H	2.35553949679453	-4.71672191125079	0.91700706259845
H	3.76046650279320	-3.78575752113276	0.38640269906846
H	2.75189063857651	-3.18643512989155	1.71507135840763
H	1.29882158990864	-4.73039530690013	-1.43802454329863
H	1.16602681516046	-3.22293284055169	-2.35213024533270
H	2.75547470618986	-3.91854434364727	-2.01173902906674
H	0.80737657250747	-2.98965809358694	0.16836459276349
H	4.70739383899004	-0.81029240915414	1.08909801603594
H	5.14153936404023	0.17258620393458	3.30072403955744
H	3.24257803226477	1.06005616566692	4.65557831368672
H	0.94589530296194	0.97345644529596	3.76387581668713
H	-2.93925719611988	-1.27632990341945	-2.78067242981208
H	-4.51650820649956	-3.07729235681993	-2.79312351095286
H	-4.09866550685563	-3.61141388809498	-1.17015859158595
H	-4.97852818218941	-2.09328583478849	-1.40190828461245
H	-2.10787084765782	-3.58800447518415	-3.25411763317619
H	-0.82982512924502	-2.50924749344472	-2.67729832850897
H	-1.53170565397654	-3.72090686696741	-1.58426145085648
H	-3.12934843245621	1.13508074141377	0.23975538025319
H	-4.98217513369706	1.63178230164796	-1.23670541916716
H	-3.64409558143543	1.08736749618645	-2.25370314847679
H	-5.00050228125803	0.00268353433571	-1.91457345975469
H	-5.37752800024192	0.57116112068621	1.05287609786030
H	-4.16451535092194	-0.49383393671072	1.78004059333268
H	-5.21887038894485	-1.09861818162806	0.49313554088162
H	-3.51358027149074	-3.32972506593427	0.73123937729176
H	-2.85436990008126	-4.64143386195160	2.70932173616653
H	-0.87792443961699	-3.93444026980875	4.05757794152547
H	0.39088847988002	-1.91692892133496	3.42545363266186
H	-1.84734497742996	0.37230306368124	3.47914821220453

Figure S49: The gas-phase optimized geometry **{TPBFeNO}^{10}** with hydrogens omitted (BP86, *S* = 0).

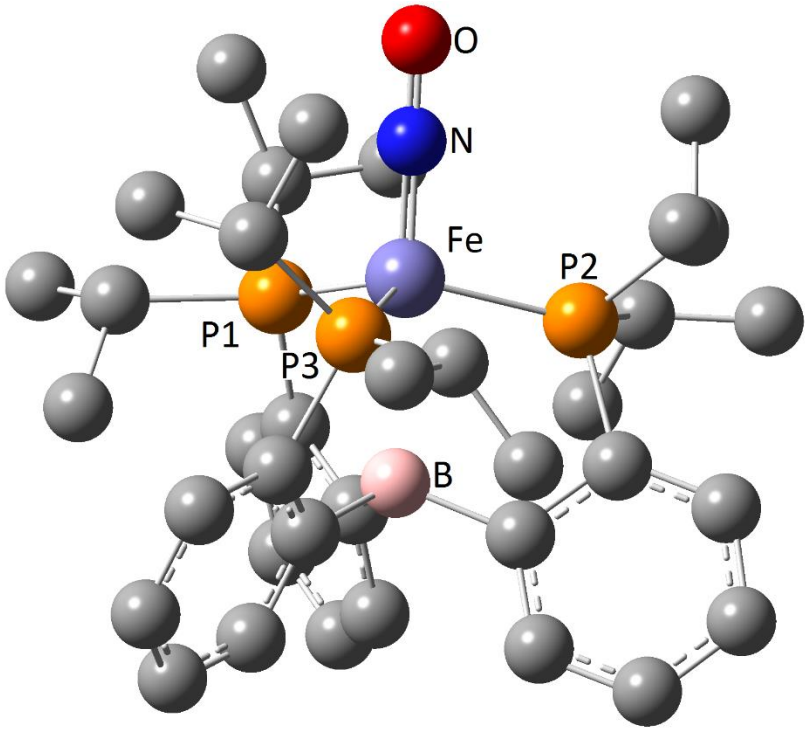


Table S20: Optimized coordinates for **{TPBFeNO}^{10}** (BP86, *S* = 0).

Fe	0.00000000	0.00000000	1.08086306
P	-0.35930958	2.14996377	0.61156741
P	-1.68226846	-1.38615311	0.61156741
P	2.04157803	-0.76381067	0.61156741
O	0.00000000	0.00000000	3.93450922
N	0.00000000	0.00000000	2.72349891
C	1.05386820	-1.13887749	-1.88449680
C	0.45936274	1.48211538	-1.88449680
C	0.74068610	3.89713919	-1.44049937
C	1.28540529	4.09532358	-2.72113820
C	0.33463466	2.61058401	-1.02756570
C	-2.42814940	-1.01548989	-1.02756570
C	0.99585716	1.72074169	-3.17435680
C	3.64991972	0.30658183	0.51071597
C	-1.51323094	-0.34323789	-1.88449680
C	-1.98813459	0.00206675	-3.17435680
C	-3.74536458	-1.30711661	-1.44049937
C	-2.10598527	4.55122155	0.48865788
C	1.40534490	2.99985572	-3.59089613
C	0.99227744	-1.72280844	-3.17435680
C	-2.90240724	2.50455889	-0.69349848

C	-1.55945221	-3.31421412	0.51071597
C	-2.09046751	3.00763228	0.51071597
C	-3.30062371	-0.28286347	-3.59089613
C	2.09351474	-1.59509412	-1.02756570
C	2.71234568	-2.07115384	1.82295157
C	-3.14984468	-1.31338334	1.82295157
C	-4.18935690	-0.93446815	-2.72113820
C	-0.71780800	-3.76583785	-0.69349848
C	-2.79612312	-1.94440026	3.18557334
C	0.43749900	3.38453719	1.82295157
C	1.89527881	-2.71699224	-3.59089613
C	3.62021525	1.26127896	-0.69349848
C	-0.28583846	3.39371379	3.18557334
C	3.00467848	-2.59002257	-1.44049937
C	1.93599364	3.12459702	2.03108036
C	4.99446612	-0.45177403	0.48865788
C	-2.88848085	-4.09944752	0.48865788
C	-3.67397722	0.11432116	2.03108036
C	3.08196158	-1.44931352	3.18557334
C	2.90395161	-3.16085543	-2.72113820
C	1.73798358	-3.23891819	2.03108036
B	0.00000000	0.00000000	-1.37218951
H	-3.68617504	-1.93804125	3.84689409
H	-2.00012209	-1.37287494	3.69113215
H	-2.45568983	-2.99102110	3.09883148
H	-3.96404845	-1.90695616	1.36315388
H	-3.99946817	0.57493402	1.08322715
H	-4.54054737	0.10547836	2.72319606
H	-2.88786488	0.75171496	2.47114599
H	-3.50959398	-3.95293893	1.38831030
H	-2.67114690	-5.18465268	0.41479118
H	-3.49276783	-3.83205521	-0.39732678
H	-1.01200921	-3.58310177	1.43431627
H	-0.56564766	-4.86373522	-0.65931427
H	0.26736104	-3.28073417	-0.72473906
H	-1.22964071	-3.52672397	-1.64288859
H	-1.32481131	0.54853467	-3.85793028
H	-3.63661000	0.02301068	-4.59105837
H	-5.22289296	-1.13949527	-3.02864609
H	-4.44702259	-1.79595870	-0.75312466
H	3.77885715	-2.95325518	-0.75312466
H	3.59827833	-3.95341035	-3.02864609
H	1.79837716	-3.16090199	-4.59105837
H	0.18736070	-1.42158759	-3.85793028
H	3.63349670	-2.47948858	1.36315388
H	2.17892674	-3.98496855	2.72319606
H	1.50182662	-3.75110805	1.08322715
H	0.79292819	-2.87682182	2.47114599
H	3.52148048	-2.22330060	3.84689409
H	2.18900563	-1.04571907	3.69113215
H	3.81814517	-0.63117922	3.09883148

H	3.60906176	0.91512520	1.43431627
H	5.17814252	-1.06292808	1.38831030
H	5.06504107	-1.10879807	-0.39732678
H	5.82561438	0.27904527	0.41479118
H	4.49494209	1.94200236	-0.65931427
H	3.66905291	0.69846189	-1.64288859
H	2.70751861	1.87190853	-0.72473906
H	0.66816544	4.74921389	-0.75312466
H	1.62461463	5.09290562	-3.02864609
H	1.83823283	3.13789130	-4.59105837
H	1.13745062	0.87305292	-3.85793028
H	2.09493669	2.12510686	2.47114599
H	2.49764155	3.17617403	1.08322715
H	2.36162062	3.87949019	2.72319606
H	0.16469456	4.16134185	3.84689409
H	-0.18888353	2.41859402	3.69113215
H	-1.36245534	3.62220033	3.09883148
H	0.33055174	4.38644473	1.36315388
H	-2.59705255	2.66797657	1.43431627
H	-3.92929442	2.92173286	-0.65931427
H	-2.97487965	1.40882564	-0.72473906
H	-2.43941220	2.82826208	-1.64288859
H	-3.15446749	4.90560741	0.41479118
H	-1.66854855	5.01586701	1.38831030
H	-1.57227324	4.94085328	-0.39732678

Figure S50: The gas-phase optimized geometry **{TPBFeNO}^{10}** with hydrogens omitted (BP86, *S* = 1).

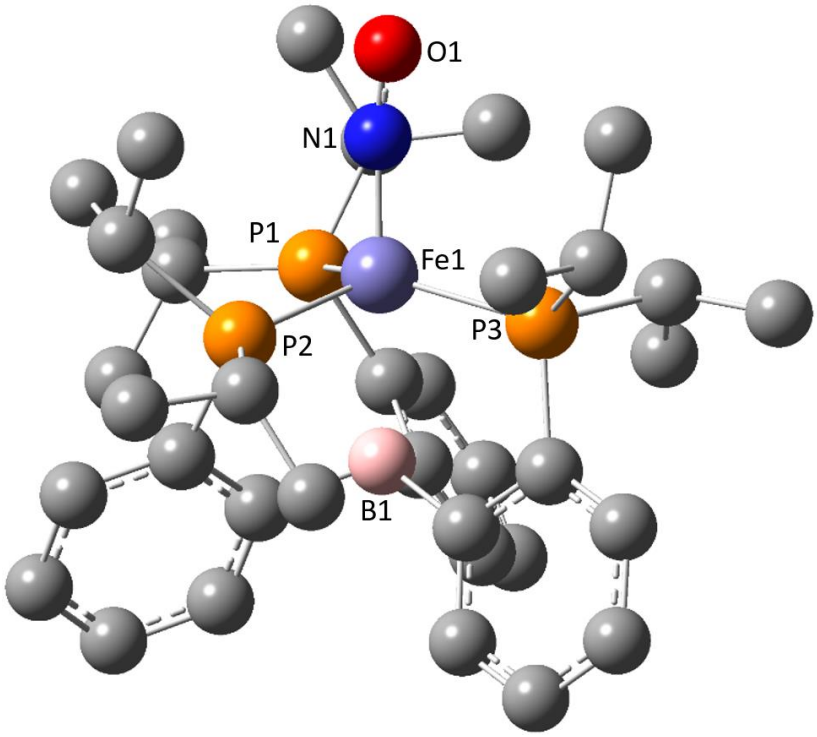


Table S21: Optimized coordinates for **{TPBFeNO}^{10}** (BP86, *S* = 1).

Fe	0.11100632022602	-0.01227245724084	-1.03354027212220
P	-2.27520008913013	-0.70857893947043	-0.67707451348215
P	0.28179005079075	2.17237822128060	-0.47099743254645
P	2.02231739531545	-1.12427107064934	-0.66144192982374
O	0.40994049354933	0.15944870897888	-3.91960210163704
N	0.05440315950304	0.02535021144337	-2.75169702995737
C	1.51535082092154	-0.42652693469077	1.92189098136386
C	-0.97570405679941	-1.44164306356321	1.64654364555831
C	-2.95833981418714	-2.83837321608682	1.12487392413599
C	-2.73386456005073	-3.64456783882000	2.25246429254337
C	-2.10673187337851	-1.75402834065662	0.82358703664247
C	-0.58114095462085	2.39987623657767	1.13888003443714
C	-0.78504461060879	-2.28403914919464	2.77819840680005
C	1.97541848321421	-3.03063226966752	-0.86951732478628
C	-0.63420759660025	1.19591790368048	1.89662635959417
C	-1.27182541640496	1.27446006748272	3.16135547658195
C	-1.15042667305047	3.59900895862734	1.61790061586857
C	-5.23361014306807	-0.66105666678389	-0.47047688260878
C	-1.63656002371060	-3.35563343906384	3.08183153254072
C	1.87020991391721	-0.16407883407247	3.26942626955753
C	-3.94822567072373	1.01555119213017	0.87835804641267
C	1.88237816873091	3.19642425276130	-0.16839210973358
C	-3.95364938600151	0.19607352691656	-0.42180687020145
C	-1.83541631748450	2.46596458042688	3.64677452245750
C	2.56159388157390	-0.91140959922681	1.08071353987436
C	3.57366506694264	-0.78278086502139	-1.70098695844186
C	-0.59134696913234	3.37531969655053	-1.64973988692934
C	-1.78409825884602	3.63547112984734	2.87120558525030
C	2.63992365626497	2.69951158604583	1.07344189192453
C	0.20146797680566	3.53043217692114	-2.96321270972323
C	-2.80383257376347	-1.92494582768050	-2.03294443766389
C	3.16846111691819	-0.37232154088350	3.76392828457276
C	1.00430983228789	-3.68367915612722	0.12440890647771
C	-3.13155388791037	-1.15702264624552	-3.32920702801579
C	3.86621661720279	-1.13059860320691	1.57312375065983
C	-1.74041417520610	-3.00249037946607	-2.29928450726668
C	3.33573714089322	-3.75021311805025	-0.77116212127702
C	1.71318349638228	4.72549192666372	-0.05608575743412
C	-2.03434119632263	2.94296802438250	-1.94795368657494
C	3.37856464310655	-1.23642541283093	-3.16213588026428
C	4.17609609885812	-0.85985042686233	2.91519463547527
C	3.98359317130243	0.69565802530405	-1.67192792728444
B	0.01267212155223	-0.18996232181500	1.32399506145669
H	-0.31280648569268	4.24746122070556	-3.63294176065554
H	0.27805058252763	2.56666510892711	-3.49253851570620
H	1.22572435741888	3.90729206523893	-2.79866097187503
H	-0.63185099908820	4.35740875019793	-1.14016512240541

H	-2.63845277394323	2.88556714673795	-1.02743659785377
H	-2.51587664352239	3.67145557360629	-2.62979110691212
H	-2.04955116276989	1.95235801996798	-2.43262212936451
H	1.29733846931438	5.19305816195043	-0.96341956175843
H	2.70322328656386	5.18792354552777	0.12723035348098
H	1.06886614303317	4.99268511020195	0.79981016720670
H	2.49925971090784	2.98353310135298	-1.06031985812848
H	3.61737399304498	3.21508552209561	1.15021237342934
H	2.81952704613745	1.61634829316362	1.05361668860648
H	2.06943862315228	2.91796271248418	1.99258869432269
H	-1.35825464559019	0.36204374128757	3.76566901210642
H	-2.33432075057287	2.47905312678040	4.62461393367681
H	-2.24507976367484	4.56390013993867	3.22968424162984
H	-1.13402017538202	4.50567693216593	1.00124773512445
H	4.65923055013880	-1.48339146481390	0.90248503183797
H	5.19630682241671	-1.01151150804540	3.28809477501619
H	3.39871478154687	-0.14488307239763	4.81297783832514
H	1.10774418291578	0.24154700614527	3.94657640675774
H	4.39531681595521	-1.37157524783803	-1.24834494992941
H	4.91361042216023	0.84166383804205	-2.25568801849614
H	4.16417322969876	1.05635565712492	-0.64649263001001
H	3.19541767800288	1.31792443195121	-2.12743492519377
H	4.30383367157862	-1.04126238205240	-3.73932056479001
H	2.55375549516867	-0.68044300907079	-3.63836639631511
H	3.15531077499265	-2.31289722383062	-3.25096883228857
H	1.57164581221777	-3.16723275018581	-1.89138747905909
H	4.05572738450349	-3.44525700272099	-1.54791053906970
H	3.79890278680805	-3.58061024634864	0.21721454545569
H	3.18138763275879	-4.84207352995123	-0.87549854854355
H	0.91091724906668	-4.76510528439267	-0.09594709977809
H	1.37088941855295	-3.57912446650374	1.15971848844434
H	0.00350242699696	-3.23374013754806	0.09062674011142
H	-3.79148211837716	-3.08261635173808	0.45509407351527
H	-3.39604658451801	-4.49117518661899	2.46976443141892
H	-1.44039923706323	-3.97523794461481	3.96698525626785
H	0.07518359488975	-2.09452699634457	3.43189653352121
H	-0.78377966086341	-2.54327252896573	-2.60068709524726
H	-1.56286874585502	-3.62475976784077	-1.40727987009778
H	-2.07640063395234	-3.66815469567633	-3.11871527290152
H	-3.44759831950741	-1.86465767400339	-4.12037199068284
H	-2.24101837467944	-0.61657764773050	-3.69190802364309
H	-3.94754976719106	-0.42577762098127	-3.19219779180200
H	-3.71932946355573	-2.43876559350643	-1.68187112058615
H	-3.98342461491492	0.90291953342583	-1.27351217972811
H	-4.88329352728897	1.60440046348647	0.95612482939677
H	-3.09770080124283	1.70974238472754	0.93514418516017
H	-3.89037493842603	0.35327253567345	1.75885021977707
H	-6.11910684828362	-0.00698239315037	-0.34043848744161
H	-5.36391607692600	-1.20082957769777	-1.42318859107035
H	-5.25085720884736	-1.39780512698296	0.35151204433305

Figure S51: The gas-phase optimized geometry **{TPBFeNO}^{10}** with hydrogens omitted (BP86, *S* = 2).

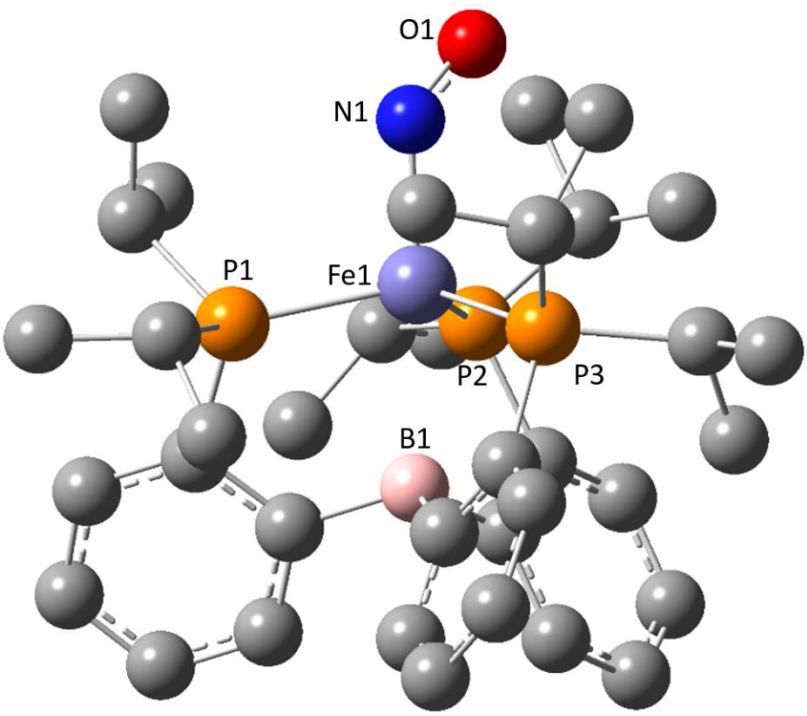


Table S22: Optimized coordinates for **{TPBFeNO}^{10}** (BP86, *S* = 2).

Fe	0.02403107679223	0.02118954548668	1.09303256445659
P	-0.44644581315016	2.24664733606115	0.58418142438951
P	-1.70148798093682	-1.44786781998235	0.63429328553523
P	2.14935156115075	-0.76800524698520	0.60903000440093
O	0.19214167966898	-0.58441257319394	3.98747212701122
N	-0.26466693787706	0.14897627823570	3.07631821746787
C	1.05409452466296	-1.15277893482877	-1.85357631288384
C	0.49073633665589	1.47592380259435	-1.85294186846572
C	0.71855325421170	3.91119539455656	-1.47562941052642
C	1.32782159289606	4.07779044435354	-2.72995339920140
C	0.30551574403684	2.63358593705301	-1.04275747977781
C	-2.41936317378777	-1.02016000733692	-1.00329778477078
C	1.09553014066111	1.68637447508133	-3.11887720178584
C	3.72788075888310	0.31755367934549	0.49314449503879
C	-1.50303095397142	-0.32076819589510	-1.83962156196572
C	-1.98369322609220	0.07247080271840	-3.11447336896855
C	-3.73895368350446	-1.28883351070136	-1.42496948389363
C	-2.16236976718484	4.62802420352074	0.38615761662723
C	1.50895893166665	2.95603912275269	-3.55437256570336
C	0.94510097643962	-1.76655693198216	-3.12744902144492
C	-2.97751738619868	2.54525073931971	-0.72857956787933

C	-1.57987357915068	-3.36377570666980	0.51262570505726
C	-2.16510143949340	3.08743266462090	0.45812010083083
C	-3.29653564341305	-0.19273825673346	-3.53819804187508
C	2.12910005723059	-1.59402799151212	-1.03014638431579
C	2.80294900807366	-2.08385645546062	1.81152430122183
C	-3.17274017793465	-1.34966020586346	1.83432877556743
C	-4.18502783439294	-0.87138263270587	-2.68970151702030
C	-0.70694920159792	-3.80377085310253	-0.67330865701918
C	-2.85183062291171	-2.02745445441027	3.18227692729395
C	0.36968264394293	3.44820169158465	1.80671483899582
C	1.83112719877251	-2.76764977808634	-3.55889754743107
C	3.65855291290080	1.30284941390074	-0.68398381685970
C	-0.39245582790046	3.47270183774089	3.14759844852574
C	3.02434140198231	-2.59634920464340	-1.45963191272428
C	1.84208959241438	3.08219733042875	2.05109679248937
C	5.06537478270416	-0.44601922775586	0.40855167407160
C	-2.91521136589183	-4.13251892525221	0.43855037113243
C	-3.61664794754605	0.10283471412395	2.06904126337657
C	3.22871311836521	-1.45859508409374	3.15575698060184
C	2.87528100573000	-3.19236480733886	-2.72256855101150
C	1.77078002741807	-3.19601317434700	2.05797445944018
B	0.01714536828234	-0.00050361523713	-1.34403571050991
H	-3.71991029381105	-1.92950775568642	3.86366547019904
H	-1.98282766461355	-1.55308304414948	3.66577845004736
H	-2.63648463032486	-3.10450854183154	3.07617408935047
H	-4.01267461292201	-1.89107117065620	1.35711040834830
H	-3.91324534370347	0.59757389767095	1.12974563669203
H	-4.48667389915590	0.12558093146546	2.75500083742747
H	-2.79742537208002	0.67845179902170	2.53245101834605
H	-3.57249140907569	-3.96651009804123	1.30712089838945
H	-2.70892043140500	-5.21988763883005	0.38466754506634
H	-3.47374979952938	-3.86364453241080	-0.47532199062725
H	-1.06343232609091	-3.64716933239985	1.44948551717281
H	-0.56852442923681	-4.90266053615329	-0.65123975282895
H	0.28348496561518	-3.32996330588038	-0.66959358002849
H	-1.18804450698483	-3.54374685428043	-1.63185282158609
H	-1.31756409229141	0.63469016937802	-3.78119367758139
H	-3.63253236693028	0.14618263880027	-4.52676479218735
H	-5.21895537660437	-1.06337085493304	-3.00123046528247
H	-4.44011566262368	-1.79886125213154	-0.75403384377945
H	3.82452184602001	-2.94476433817763	-0.79604214024446
H	3.55825934496880	-3.98904203959238	-3.04115754492171
H	1.69630510231269	-3.23013673565029	-4.54526658799443
H	0.11724615099334	-1.47520663844023	-3.78599484916900
H	3.69045669287987	-2.53894697627690	1.33048573059877
H	2.19975713872068	-3.96229375583685	2.73324622253171
H	1.47387915668706	-3.69636708041934	1.12222235458058
H	0.86993111126658	-2.78445394923331	2.54351035420946
H	3.61536517205090	-2.25091969661393	3.82621326456082
H	2.36253418646768	-0.98960536274031	3.65378343589371
H	4.02459310166948	-0.70248120746248	3.04500759702086

H	3.71257228251910	0.89789710140581	1.43509277496999
H	5.25830038457103	-1.10031697561330	1.27382632436521
H	5.11016481212187	-1.05976912915339	-0.50823322171121
H	5.89828379741522	0.28218485543387	0.35330749615666
H	4.53755343543057	1.97636779933576	-0.66077517855032
H	3.67074557387771	0.76480821645546	-1.64718568380895
H	2.74924903352190	1.91801474668239	-0.66831275349664
H	0.59857558307013	4.78177547962380	-0.81992745074210
H	1.66846841183267	5.06936408540364	-3.05144221730323
H	1.98926716254600	3.06859557171802	-4.53502893917018
H	1.27719095082891	0.82093619983055	-3.76846168552839
H	1.91807844692506	2.06726477828386	2.47872954689518
H	2.43373959178389	3.11705249253096	1.12212794218900
H	2.29445196892231	3.79189890099009	2.77140841548589
H	0.12356373088037	4.14531698722986	3.86045510136074
H	-0.42075923414752	2.45735269145246	3.58185839588516
H	-1.43039710503737	3.83238209978422	3.04314049810131
H	0.33730360228933	4.45741138460912	1.35156597357676
H	-2.66830258436491	2.77987165037461	1.39420395183463
H	-3.99713721642379	2.97746397015704	-0.71244199669942
H	-3.06486465500469	1.45056480770770	-0.71610918633769
H	-2.50722427191365	2.82493714400480	-1.68683050354445
H	-3.20706848804302	4.99320761773994	0.33602231473292
H	-1.68716615986766	5.11113489013671	1.25520435395144
H	-1.65230194860929	4.97883009600677	-0.52811208431456

Figure S52: The gas-phase optimized geometry **{TPBFeNO}^{10}** with hydrogens omitted (B3LYP, *S* = 0).

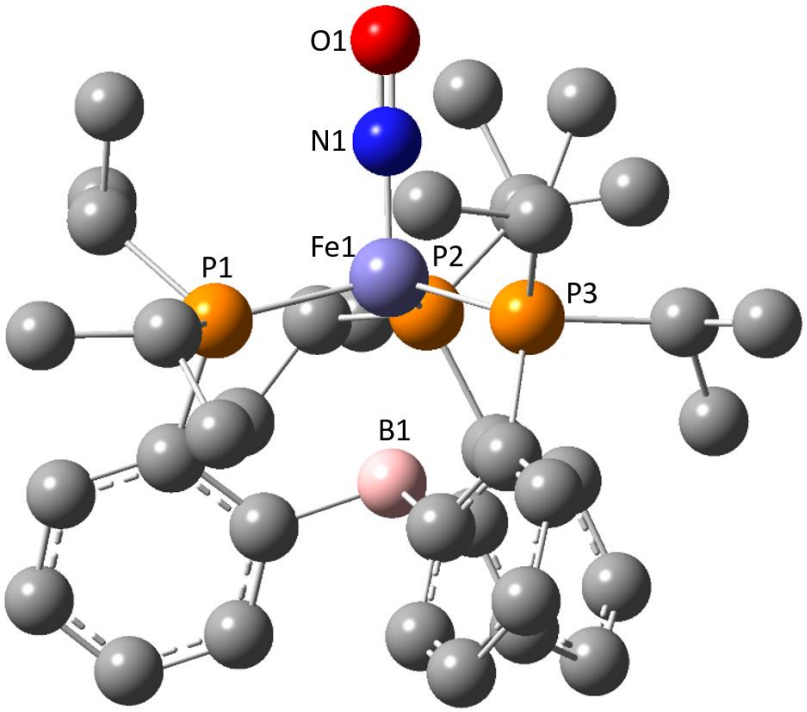


Table S23: Optimized coordinates for **{TPBFeNO}^{10}** (B3LYP, S = 0).

Fe	0.00001620117003	-0.00013318003729	1.07884344750368
P	-0.36260990278241	2.16545489233766	0.60779105186891
P	-1.69391274939118	-1.39700567070158	0.60751625850378
P	2.05653300154635	-0.76909574035703	0.60770725077931
O	0.00035797158094	-0.00043122564934	3.90809044310830
N	0.00017156623012	-0.00022038365582	2.70309316623051
C	1.05670735280090	-1.14113062385876	-1.88200653822934
C	0.45987919691423	1.48548588929740	-1.88193653891976
C	0.73326870216308	3.88877908304368	-1.44690900545319
C	1.27331941067570	4.08707789838729	-2.71977668009674
C	0.33275451190564	2.60934952854322	-1.03150985341929
C	-2.42600557058081	-1.01696518301425	-1.03179379512957
C	0.99730363751945	1.72383375322882	-3.16383172128562
C	3.65442318137305	0.30083307348807	0.51205059235762
C	-1.51622704764113	-0.34495339889921	-1.88218803870180
C	-1.99130343357732	0.00141364026435	-3.16405775056456
C	-3.73435857712308	-1.30957884063516	-1.44717523559127
C	-2.11357849894938	4.55609767107000	0.50853691120773
C	1.39916862670034	2.99550181597798	-3.58117247599602
C	0.99432704759985	-1.72555602587293	-3.16396464098189
C	-2.90852540822922	2.52928677090028	-0.69070146500524
C	-1.56655853168502	-3.31595268151625	0.51244990454997
C	-2.08802622323266	3.01460480451131	0.51240295184902
C	-3.29357675519450	-0.28618489214900	-3.58139177122344
C	2.09333818030943	-1.59336040316860	-1.03152104669211
C	2.71524015463026	-2.07774712887724	1.81242244128659
C	-3.15694238438398	-1.31282401333955	1.81167903943856
C	-4.17607034280521	-0.94086731247377	-2.72001169113322
C	-0.73464020289579	-3.78447123293052	-0.68949391303799
C	-2.80295442935545	-1.92039938757682	3.18233173769407
C	0.44134425522714	3.39058542574469	1.81222576737134
C	1.89448260135683	-2.70955488181592	-3.58139976800736
C	3.64340267414830	1.25527914797299	-0.69002841727315
C	-0.26139158790459	3.38639404353129	3.18309189415210
C	3.00092164232055	-2.58008035381797	-1.44701470253633
C	1.94259963299702	3.15083864814544	2.00716411770814
C	5.00203240206473	-0.44798233513439	0.50633889094622
C	-2.88910979259357	-4.10825462626162	0.50677509063877
C	-3.69793385315156	0.10784922373236	2.00694324409715
C	3.06541355919533	-1.46683231263404	3.18259939966609
C	2.90257736550941	-3.14669323806064	-2.71999167405574
C	1.75499229550781	-3.25606070699521	2.00920933468490
B	0.00013462985454	-0.00014614248556	-1.37529322405651
H	-3.69114590850387	-1.91571124516294	3.83136415803116
H	-2.02229823071468	-1.33931284334090	3.68125715275290
H	-2.45499447234829	-2.95634781482523	3.11223194952913

H	-3.96387212248962	-1.91025370716838	1.36941433282872
H	-4.01533196046440	0.55922350208856	1.06239048916580
H	-4.56826375031913	0.08703534624162	2.67967067298663
H	-2.93715881786136	0.75204859182782	2.45767781806621
H	-3.49827145051531	-3.95846202988054	1.40245442945667
H	-2.66512920265846	-5.18340996018550	0.44439347680285
H	-3.49888594637956	-3.85827001749289	-0.36911900395880
H	-1.01942985087332	-3.58094194386365	1.42505992772298
H	-0.58806996579321	-4.87353620236033	-0.63865204426424
H	0.24483337048692	-3.31198557794612	-0.73351246663055
H	-1.24737392489078	-3.56190599818565	-1.63201937415443
H	-1.33656833508911	0.54384555677795	-3.84331154157041
H	-3.62497046706756	0.01646065527324	-4.57419676231147
H	-5.19892998183425	-1.15092194339339	-3.02793417091137
H	-4.42956952611042	-1.79966926654675	-0.76950045864253
H	3.77303929472243	-2.93717643723421	-0.76946907839852
H	3.59595963556689	-3.92740910822509	-3.02802467329364
H	1.79817579402429	-3.14763007824240	-4.57432165035603
H	0.19740394878363	-1.42944419531250	-3.84332217511209
H	3.63566720878184	-2.47860687192609	1.36993953648856
H	2.20835549269134	-3.99895824427219	2.68228820234937
H	1.52200835685883	-3.75744329765505	1.06527634877211
H	0.81714522085303	-2.91853822290123	2.46030117631435
H	3.50437686665138	-2.23857971714885	3.83211007033402
H	2.17240291496175	-1.07979168020866	3.68137543267264
H	3.78983920049114	-0.64869070817185	3.11192214530955
H	3.61010541194056	0.90744970923571	1.42446798735469
H	5.17715965047504	-1.05032278879080	1.40204121677702
H	5.09048671221217	-1.10117459194065	-0.36944883600765
H	5.82097332159095	0.28376205743879	0.44377916609767
H	4.51230373561395	1.92799080017396	-0.63903808357952
H	3.70806068708162	0.70000131361805	-1.63251647203086
H	2.74353088103354	1.86582755566585	-0.73419342307905
H	0.65623198999704	4.73585011484761	-0.76920381356706
H	1.60259790243693	5.07799725220483	-3.02773044491481
H	1.82681485059119	3.13126085013089	-4.57402980534103
H	1.13963001761170	0.88566267323852	-3.84319095431519
H	2.12179880367993	2.17023612932852	2.45800404420322
H	2.49203778920293	3.20091579671138	1.06257298000054
H	2.35866236265737	3.91561758108843	2.67982813064297
H	0.18576882070396	4.15378348892731	3.83217649120485
H	-0.14675369671529	2.41980887884343	3.68166660337127
H	-1.33289887060096	3.60132216815744	3.11344219168863
H	0.32608643020718	4.38818963790119	1.37044779424590
H	-2.59156761137385	2.67199745072959	1.42426148843503
H	-3.92607259460461	2.94404920429939	-0.63886319854076
H	-2.98597092795572	1.44469552291686	-0.73746516980102
H	-2.46026728917641	2.86559502758468	-1.63239312353770
H	-3.15673020382481	4.89926307964496	0.44455307022270
H	-1.68126971764619	5.00783884341150	1.40565919731635
H	-1.59064636592254	4.96058233581540	-0.36578576507837

Figure S53: The gas-phase optimized geometry **{TPBFeNO}^{10}** with hydrogens omitted (B3LYP, *S* = 1).

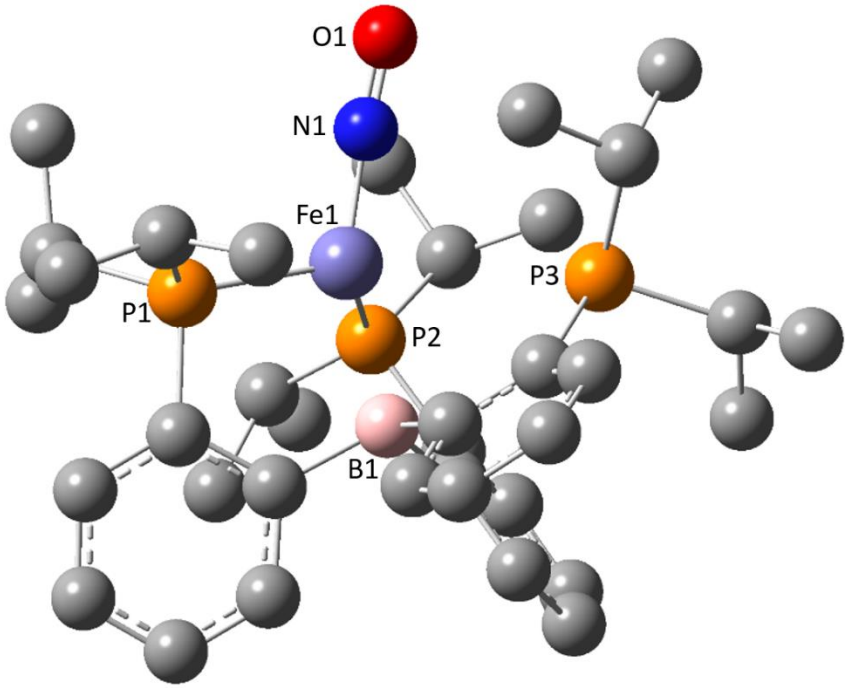


Table S24: Optimized coordinates for **{TPBFeNO}^{10}** (B3LYP, *S* = 1).

Fe	0.09459425524079	0.45979569863476	1.18040179232624
P	-0.08063449284620	2.75701257469135	0.66214840572250
P	-1.88649296212150	-2.30758626098638	0.42885888132077
P	2.26613875892195	-0.50472231358399	0.86764176436616
O	-0.84552039852602	0.02404388245051	3.94284508978998
N	-0.42735107707366	0.23298650176962	2.83085415115880
C	0.92162413193232	-1.08695113339624	-1.47038103021797
C	0.41825280011733	1.53128200713476	-1.76497228853565
C	0.75028015601654	3.98246693513986	-1.76965311156123
C	1.23048218615153	3.95570687945986	-3.07739277389209
C	0.36521895192005	2.79854522171908	-1.11202997193816
C	-2.47407764932600	-1.27358744501200	-0.99400282609548
C	0.93840570397820	1.55386104585004	-3.08102850213510
C	3.91318799161731	0.41555847821934	0.63213553429185
C	-1.64293639533353	-0.22897963137937	-1.53181166520028
C	-2.24683417903384	0.52873471504014	-2.57362695401690
C	-3.78268147165768	-1.46500350786354	-1.47479876566155
C	-1.98999893988433	4.91449372955244	0.26415020622372
C	1.33364571360928	2.72388201738225	-3.72989242907341
C	0.76944952688845	-1.79893254540511	-2.68462039471516
C	-2.89188181101204	2.56566371086613	0.28179552351465
C	-1.97134878605368	-4.11827601002968	-0.16192350940441
C	-1.81115014600542	3.49984396427092	0.83972918176582

C	-3.54003450232525	0.31900710775152	-3.04898326229521
C	2.05280474668992	-1.44811907631245	-0.68832498367443
C	2.72361500959380	-1.78032004122056	2.16915199020638
C	-3.38007097141695	-2.30818567909976	1.59597716862886
C	-4.33033469296210	-0.68779012964667	-2.49586623171632
C	-0.77885446666589	-4.45150125835909	-1.06957798553965
C	-3.02999788815232	-3.08304711640695	2.88043368573253
C	0.93158274720249	4.14486713347165	1.46236746814809
C	1.66402440338027	-2.78193369943460	-3.10886193719890
C	3.90348083283515	1.20215269962029	-0.68816062025245
C	0.55670228796782	4.28435575958251	2.94892993552515
C	2.93986062306025	-2.45948995242817	-1.09793097945671
C	2.43946149228376	3.89819066514251	1.32804729833555
C	5.21036474874247	-0.40642560300390	0.72894276793487
C	-3.26316913507232	-4.66213794085783	-0.79377959025635
C	-3.83835275523558	-0.88724059525265	1.95813552527621
C	3.00964834550105	-1.08585141488629	3.51286408543901
C	2.75624561755759	-3.12755572977226	-2.30861502059214
C	1.62889152963321	-2.84425411804091	2.33655677328092
B	-0.11310300868873	0.12577244255840	-1.07624569996800
H	-3.89789697922477	-3.11215324921747	3.55516924944028
H	-2.20880601199000	-2.59193465371392	3.41541201193620
H	-2.73474754988511	-4.12038503545389	2.68221992678210
H	-4.22318693126549	-2.81664832884309	1.10782575941246
H	-4.15743657952482	-0.32960572257311	1.07295096722508
H	-4.68941389186779	-0.93412950334038	2.65376246476029
H	-3.03715094194249	-0.32728564680748	2.45089204171135
H	-4.14700179990152	-4.49957466461386	-0.16618215607586
H	-3.17358331948668	-5.74740774932355	-0.95455575223526
H	-3.45115770138899	-4.20036240112953	-1.76913397761195
H	-1.81589351093386	-4.65663187002241	0.78493996006111
H	-0.71610705842741	-5.53711496104783	-1.23812355057009
H	0.17074007525389	-4.11525941624619	-0.64270379947811
H	-0.88164022594812	-3.96883903047432	-2.04641219191195
H	-1.66734084055446	1.32371557324271	-3.03331119098753
H	-3.92722985574335	0.94459340397273	-3.85344932503789
H	-5.34757894094110	-0.86413616950197	-2.84119160930672
H	-4.40808507649106	-2.23022046879379	-1.02412689121142
H	3.77381299653723	-2.74520535568611	-0.46045361099226
H	3.44713995479841	-3.91075690435220	-2.61533466047090
H	1.50156800565120	-3.29205059307140	-4.05800696207569
H	-0.09053049138606	-1.57068470475549	-3.31167177789484
H	3.63834057219001	-2.28690000309109	1.83331225718764
H	1.93547686393633	-3.57415610659576	3.09979559013340
H	1.44321908145267	-3.38352665244245	1.40286802621403
H	0.68214659894940	-2.39510764366367	2.65068808545967
H	3.29920689659590	-1.82955500469112	4.26858789704373
H	2.11556980468911	-0.56633686287457	3.87482046876758
H	3.82135066004327	-0.35168874254804	3.44274071145710
H	3.91513284123638	1.13861564101741	1.45846170087641
H	5.32399074462916	-0.91955443474803	1.68934017924355

H	5.27089856647888	-1.15494299636722	-0.06895530890621
H	6.07584684632274	0.26176454321516	0.61114876076158
H	4.76661623715150	1.88166173125221	-0.72811198505917
H	3.96879783804287	0.52232052281348	-1.54481427468063
H	2.99450733688168	1.79346260917000	-0.81346172040093
H	0.69776888246015	4.93611491933128	-1.24864212615053
H	1.53418805672991	4.87688330983682	-3.57160190832121
H	1.71909714037375	2.67664803799108	-4.74807731609163
H	1.03002196179450	0.61250489892532	-3.61777199262629
H	2.72158807565012	2.95973993270806	1.81834140451667
H	2.75466145172312	3.84257941452594	0.28232069397486
H	3.00001975013356	4.71237248691464	1.80947025911292
H	1.21956985939672	5.01044756969392	3.44030755195731
H	0.66316175482574	3.32357039837802	3.46812013824787
H	-0.47247732029369	4.62949781709641	3.09365304289617
H	0.69806359056536	5.09048207056234	0.95562533775479
H	-1.94988608724149	3.54699313604543	1.92851789858438
H	-3.88789404451518	2.95582335362294	0.53674683309148
H	-2.80293012060362	1.55676152651401	0.68973741654961
H	-2.83082586798029	2.48218416577486	-0.80718892108591
H	-3.02388643517473	5.25299286595492	0.42224277840620
H	-1.33056964187866	5.65491123132454	0.73061065204334
H	-1.80238206135134	4.92518176817621	-0.81595557201672

Figure S54: The gas-phase optimized geometry **{TPBFeNO}^{10}** with hydrogens omitted (B3LYP, *S* = 2).

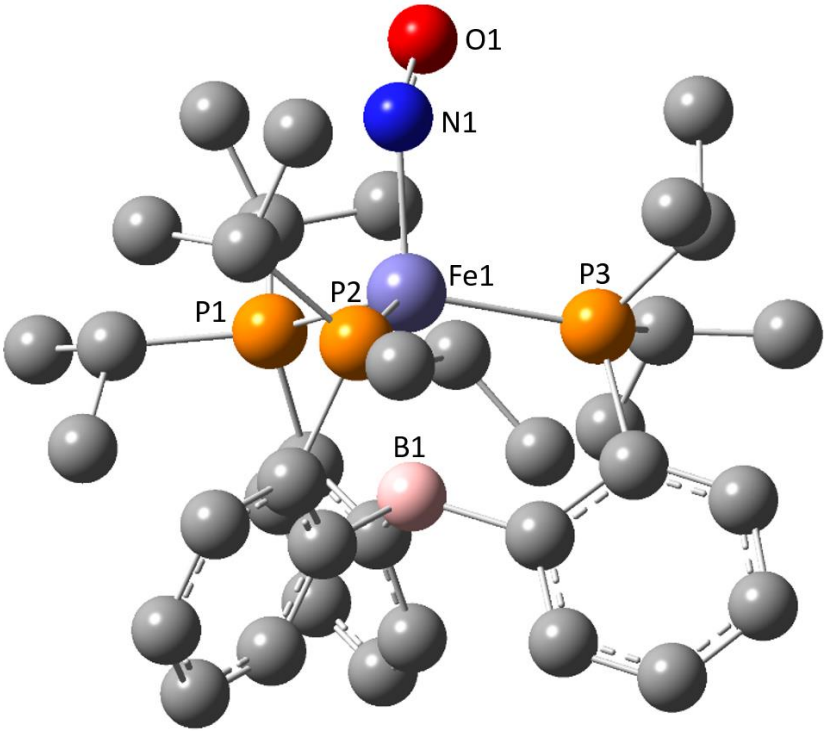


Table S25: Optimized coordinates for **{TPBFeNO}^{10}** (B3LYP, *S* = 2).

Fe	0.03634500	0.00929100	-1.08301500
P	-2.31240300	-0.33635100	-0.72185200
P	0.88774200	2.17968200	-0.52046300
P	1.48051000	-1.82022400	-0.55149300
O	0.93882400	0.23969400	-4.02524200
N	0.04982400	0.00678800	-3.18727000
C	1.31676700	-0.63593000	1.91045200
C	-1.35391700	-0.97712900	1.75812500
C	-3.54587900	-1.99104300	1.27155200
C	-3.56103400	-2.63424600	2.50985000
C	-2.46519300	-1.17583800	0.89694200
C	0.11184500	2.62435300	1.08021000
C	-1.41059800	-1.64060600	3.00404300
C	0.99468700	-3.66542400	-0.48781800
C	-0.31905900	1.50869600	1.84524200
C	-0.95410100	1.80546300	3.07175100
C	-0.09514800	3.93983800	1.52704700
C	-5.12523200	0.50182400	-0.68995000
C	-2.48383000	-2.45067700	3.37942800
C	1.79320100	-0.32945100	3.20430200
C	-3.49932100	1.93624400	0.54449800
C	2.70844800	2.69245700	-0.27790500
C	-3.66926900	1.00149300	-0.66137000
C	-1.16021400	3.11212400	3.51808800
C	2.12682700	-1.50745500	1.13663700
C	3.01462300	-1.94904400	-1.64622200
C	0.34246800	3.52955700	-1.72417900
C	-0.73355200	4.19183600	2.74232200
C	3.34873700	1.98052400	0.92188300
C	1.15598600	3.47563800	-3.03101100
C	-3.08706200	-1.51084500	-1.97976600
C	2.99294400	-0.83800400	3.70595300
C	-0.01709600	-3.95006100	0.63057300
C	-3.25086600	-0.81293000	-3.34330900
C	3.33261900	-2.02215700	1.64015000
C	-2.25528500	-2.78904200	-2.15217600
C	2.14736000	-4.67933900	-0.36980200
C	2.98532100	4.20153900	-0.14972600
C	-1.15569400	3.42637900	-2.04195700
C	2.66305200	-2.49901900	-3.04171700
C	3.77425600	-1.68870800	2.92169800
C	3.73485800	-0.60141000	-1.79275100
B	-0.08899700	-0.02854300	1.34165400
H	0.79507400	4.25154500	-3.72129100
H	1.04964700	2.50538400	-3.52635400
H	2.22437000	3.65538100	-2.87008700
H	0.51711100	4.50045200	-1.24255800
H	-1.77118100	3.52082200	-1.14279700
H	-1.44695900	4.22883100	-2.73476800
H	-1.38219400	2.46840300	-2.52235000

H	2.64414800	4.78428300	-1.00963300
H	4.06804000	4.36597600	-0.05257200
H	2.51529700	4.61241700	0.75081700
H	3.19831600	2.32976100	-1.19073500
H	4.42501700	2.20208800	0.95406600
H	3.22357100	0.89909100	0.88675000
H	2.90833300	2.32735800	1.86276600
H	-1.32013200	0.98435700	3.68453200
H	-1.66555000	3.28868600	4.46679600
H	-0.90504000	5.21511000	3.07061900
H	0.21707200	4.78099200	0.91303400
H	3.95292500	-2.66590700	1.02132400
H	4.71985200	-2.07719500	3.29487500
H	3.32476100	-0.56046400	4.70569300
H	1.21670200	0.35071500	3.82784800
H	3.70757200	-2.64726800	-1.15937100
H	4.63493100	-0.72741400	-2.41150100
H	4.04819100	-0.19810900	-0.82574600
H	3.09059100	0.13022400	-2.29016900
H	3.58215300	-2.60921100	-3.63496200
H	2.00309900	-1.80847800	-3.57455900
H	2.18024400	-3.48134700	-3.00289100
H	0.49213200	-3.83043800	-1.44950000
H	2.86512500	-4.62338300	-1.19273600
H	2.69349000	-4.54789100	0.57113400
H	1.73602400	-5.69896400	-0.36437500
H	-0.37135500	-4.98820800	0.55714500
H	0.44345500	-3.82326800	1.61616600
H	-0.88270400	-3.28997300	0.59189300
H	-4.37263400	-2.15212500	0.58382800
H	-4.39451700	-3.27770300	2.78455200
H	-2.47452600	-2.94948200	4.34776200
H	-0.57376400	-1.53661500	3.69133700
H	-1.25232700	-2.54831200	-2.51981900
H	-2.16024400	-3.34464600	-1.21503500
H	-2.73529100	-3.44981100	-2.88816700
H	-3.68338100	-1.51476100	-4.07045900
H	-2.27642700	-0.48418700	-3.72154500
H	-3.91216200	0.05910700	-3.29646400
H	-4.07823200	-1.80235600	-1.60865000
H	-3.49129200	1.58698700	-1.57249500
H	-4.22537700	2.75916400	0.48068700
H	-2.50047100	2.36680100	0.60751400
H	-3.68211200	1.40165500	1.48271000
H	-5.80645400	1.36449900	-0.67447900
H	-5.36733800	-0.08710200	-1.57894200
H	-5.35252400	-0.10363200	0.19470700

Figure S55: The gas-phase optimized geometry **{TPBFeNO}^{10}** with hydrogens omitted (B3LYP, BS).

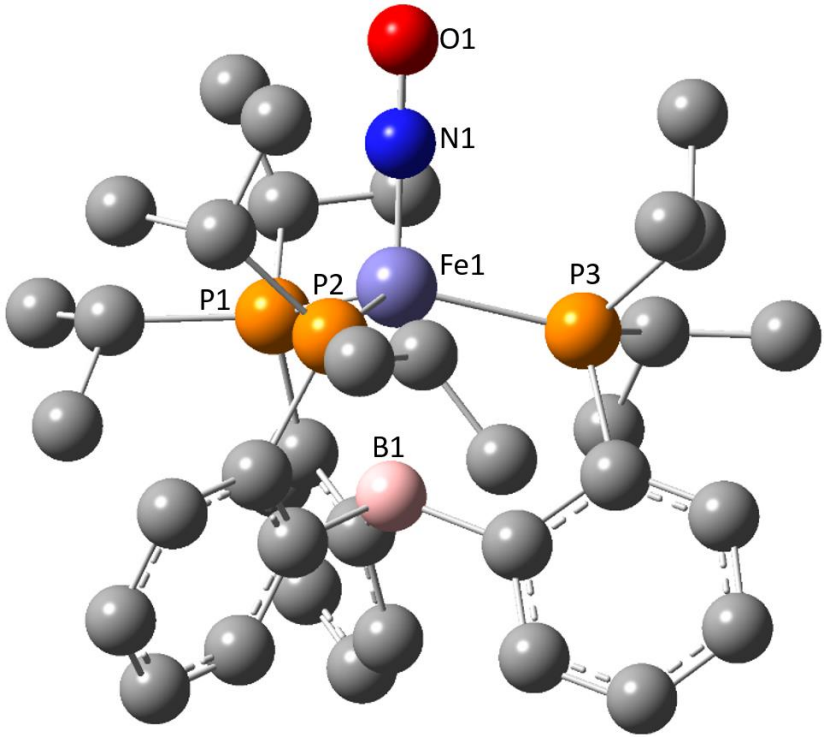


Table S26: Optimized coordinates for **{TPBFeNO}^{10}** (B3LYP, BS).

Fe	0.00007314625705	-0.00044703818324	1.08452402008421
P	-0.37847066878514	2.19393477905176	0.60952375939663
P	-1.71098825053215	-1.42516902513110	0.60909825952645
P	2.08928252855682	-0.77011535769672	0.60949697681624
O	0.00157589034576	-0.00048753885199	3.97642685815583
N	0.00054379622984	-0.00043429217967	2.76749859577402
C	1.05543061381374	-1.14303375460444	-1.87138329446754
C	0.46231674932963	1.48498469713318	-1.87118693477564
C	0.72256080164700	3.89409293824803	-1.45531109521691
C	1.27420306517156	4.08385310126456	-2.72435540295833
C	0.32281000968065	2.61680487098578	-1.03193669754809
C	-2.42752692557043	-1.02964581903284	-1.03253846994877
C	1.01252133899435	1.71558241253192	-3.14954133879615
C	3.68373586996662	0.29998887646802	0.51434710245797
C	-1.51693177467427	-0.34289798152031	-1.87160948724884
C	-1.99158479653600	0.01865423082582	-3.14992335715498
C	-3.73350843842004	-1.32205425410392	-1.45614671150224
C	-2.12982361440768	4.58165008789087	0.50508118344403
C	1.41339783483678	2.98498683809901	-3.57434249268177
C	0.98010224593379	-1.73437725112397	-3.14993839574906
C	-2.92079434684436	2.54582419106872	-0.68632725559857
C	-1.58316969465446	-3.34139639647527	0.51469507137471

C	-2.10212492257837	3.04064411083069	0.51424420648271
C	-3.29130663601805	-0.26877659566395	-3.57494270830701
C	2.10504867800747	-1.58870587068534	-1.03203948644625
C	2.74168193376910	-2.08686593285444	1.80742375856374
C	-3.17796037313243	-1.33054716186776	1.80636426761318
C	-4.17345792261185	-0.93897865886205	-2.72520709982005
C	-0.74298455261017	-3.80428780165663	-0.68375392871599
C	-2.82696158566098	-1.93080317853991	3.18089128169523
C	0.43606535012745	3.41728369016268	1.80730686204747
C	1.87883926631397	-2.71629626050989	-3.57492950702825
C	3.66258177884799	1.25890080758710	-0.68414082991625
C	-0.25841194530989	3.41097946948377	3.18224631730905
C	3.01121404371901	-2.57359188986188	-1.45562445189190
C	1.93771973351619	3.16882812727364	1.99031864195334
C	5.03226810637126	-0.44622213776692	0.50204851083239
C	-2.90454042769887	-4.13476591089830	0.50264597202715
C	-3.71095532581340	0.09496816540698	1.99048408653562
C	3.08771724332182	-1.48174673485333	3.18111877455015
C	2.89983428960673	-3.14569551667390	-2.72490971054128
C	1.77334023768403	-3.26060876438807	1.99387707333304
B	0.00024917995250	-0.00030644434887	-1.36390548468324
H	-3.71310445798161	-1.91163962860797	3.83232595496789
H	-2.03853383582753	-1.35406984239621	3.67287211558776
H	-2.49032828441576	-2.97108263887607	3.11743316162266
H	-3.98658849298431	-1.92775398457631	1.36669259227032
H	-4.02744721146549	0.53971260842630	1.04250648980470
H	-4.58002977389189	0.08510172879291	2.66500763457093
H	-2.94558107931376	0.73896061710809	2.43401604802727
H	-3.51848402353063	-3.98277310812991	1.39487236836047
H	-2.68031878450620	-5.21005619092023	0.44344606885970
H	-3.50966295174511	-3.88594268212223	-0.37688734619238
H	-1.03946390959288	-3.60586189782337	1.42994239687715
H	-0.58609068154980	-4.89173488262852	-0.63107960370631
H	0.23191345320279	-3.32158628661468	-0.72522124723755
H	-1.25478402120086	-3.58747366551579	-1.62810643408667
H	-1.33671767815529	0.57143303499933	-3.82063189566963
H	-3.62084343020559	0.04523529353956	-4.56486945134506
H	-5.19434512583628	-1.14992364765788	-3.03898346409397
H	-4.42822696663797	-1.82422972029531	-0.78679768001963
H	3.79332434933266	-2.92439474456879	-0.78626347575157
H	3.59300361415319	-3.92429367192308	-3.03870884965787
H	1.77201852028956	-3.15827047885905	-4.56505885880836
H	0.17439462257749	-1.44316179898293	-3.82094276997646
H	3.66255268468924	-2.48943404422443	1.36720565778672
H	2.21715978233958	-4.00800369564394	2.66828537532095
H	1.54467052755203	-3.75773058710380	1.04663855901878
H	0.83385562387420	-2.91894536266821	2.43868271827403
H	3.51326099795604	-2.25873262824961	3.83316220618294
H	2.19492022236016	-1.08539679956984	3.67315856625786
H	3.82166289454031	-0.67144719624496	3.11643889757396
H	3.64026355824653	0.90328222114895	1.42950587675189

H	5.20831051545513	-1.05393211479054	1.39407856748442
H	5.11992057399545	-1.09444432591378	-0.37753774223111
H	5.85065618585610	0.28642326844041	0.44291199135585
H	4.52446929811918	1.94036104005187	-0.63159585381843
H	3.73173230290815	0.70743794581644	-1.62856304013292
H	2.75565680099710	1.85976870116666	-0.72527128239235
H	0.63493951098996	4.74666355969448	-0.78579024601327
H	1.60185329842921	5.07352566016314	-3.03797950809869
H	1.84989079812688	3.11359221451223	-4.56431644913250
H	1.16355985360494	0.87225809784874	-3.82054466238582
H	2.11521606691921	2.18381773330056	2.43251451797625
H	2.48052107796447	3.22298446852509	1.04212092024064
H	2.36246369952552	3.92642296750880	2.66561244453379
H	0.20051041249337	4.16883845958719	3.83421123911600
H	-0.15140736800935	2.43942174423381	3.67306890285597
H	-1.32799374101006	3.63802482982714	3.11969329838979
H	0.32122597409737	4.41636965966296	1.36861109842859
H	-2.60403746574942	2.69979547792467	1.42815330281112
H	-3.94185739611905	2.95159806881844	-0.63387227782249
H	-2.98792291358823	1.46009585801179	-0.73047045565223
H	-2.47662182205920	2.88371589954310	-1.62940516513036
H	-3.17330392473643	4.92433575618747	0.44409309390765
H	-1.69381479019558	5.03597267965061	1.39920158119342
H	-1.61002863042994	4.98346222443880	-0.37235514602989

Figure S56: A molecular orbital diagram for **{TPBFeNO}^{8}** picturing select valence orbitals. The orbitals drawn in red correspond to those depicted (isovalue = 0.05) on the right. The orbitals are denoted by their d-orbital parentage. Energies are relative to the HOMO (d_{z^2}) which was set to be 0 eV.

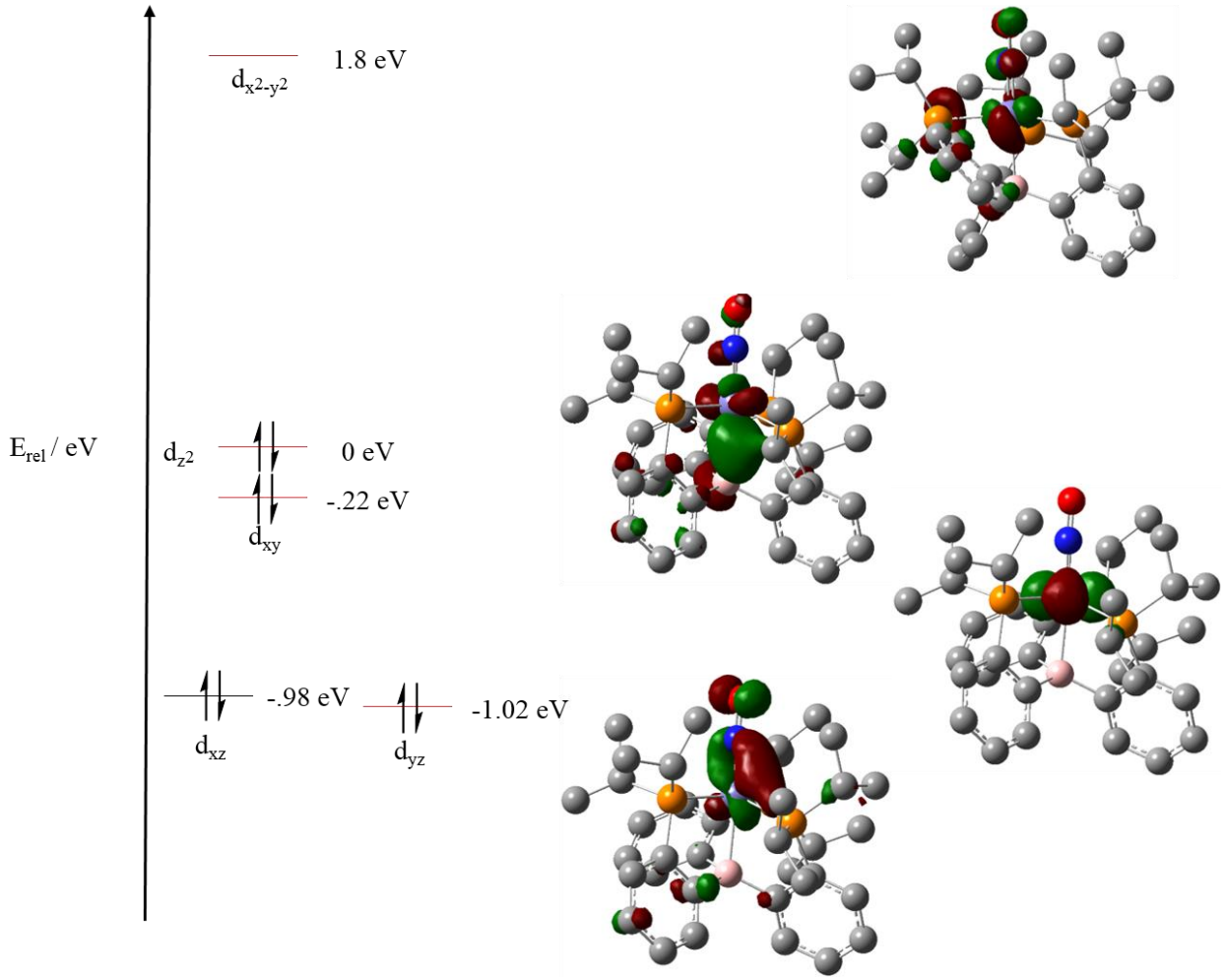


Figure S57: A molecular orbital diagram for **{TPBFeNO}^{10}** picturing select valence orbitals. The orbitals drawn in red correspond to those depicted (isovalue = 0.05) on the right. The orbitals are denoted by their d-orbital parentage. Energies are relative to the HOMO (d_{xy}) which was set to be 0 eV.

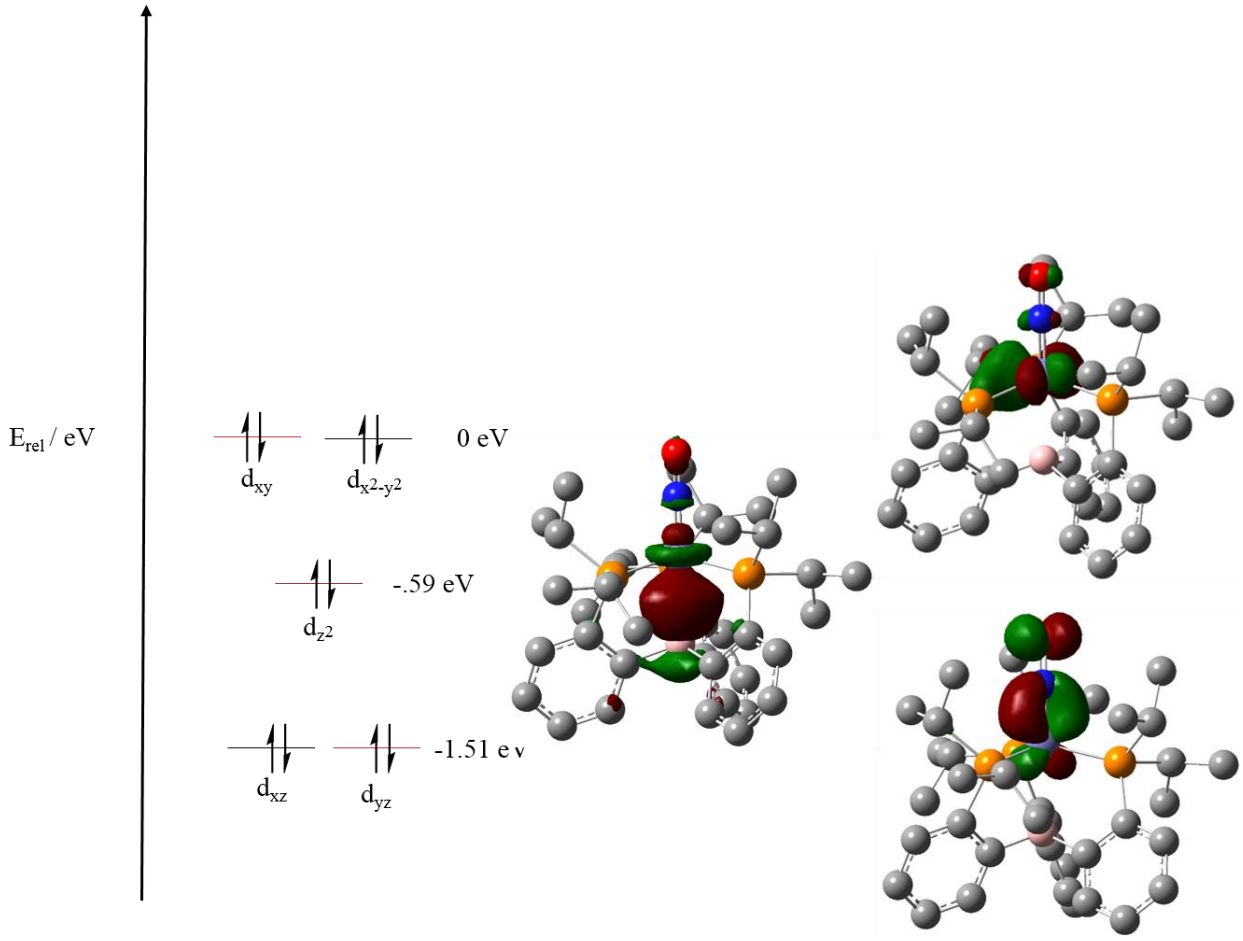


Table S27: Comparison of crystallographically determined bond lengths and Wiberg Bond Indices for **{TPBFeNO}$^{8\text{-}10}$**.

Compound	Fe-N Bond Length (Å)	Fe-B Bond Length (Å)	N-O Bond Length (Å)	Expt. ν(NO) (cm^{-1})	Fe-N Bond Order	Fe-O Bond Order	Fe-B Bond Order	N-O Bond Order	Calc. ν(NO) (cm^{-1})
{TPBFeNO}^{8}	1.655(3)	2.311(3)	1.160(4)	1745	1.5166	.4981	.3558	1.8163	1756
{TPBFeNO}^{9}	1.6712(5)	2.4451(6)	1.1901(7)	1667	1.5958	.5156	.4402	1.7244	1696
{TPBFeNO}^{10}	1.6505(13)	2.4455(16)	1.2207(16)	1568	1.7049	.4832	.4708	1.6260	1614

Figure S58: A molecular orbital diagram for **{TPBFeNO}^{9}** picturing selected valence orbitals from the β-spin manifold. The orbitals are denoted with their d-orbital parentage. Energies given are relative to the HOMO ($d_{x^2-y^2}$) for the β-spin set which was set to be 0 eV. The depicted orbitals are shown at an isovalue of 0.05.

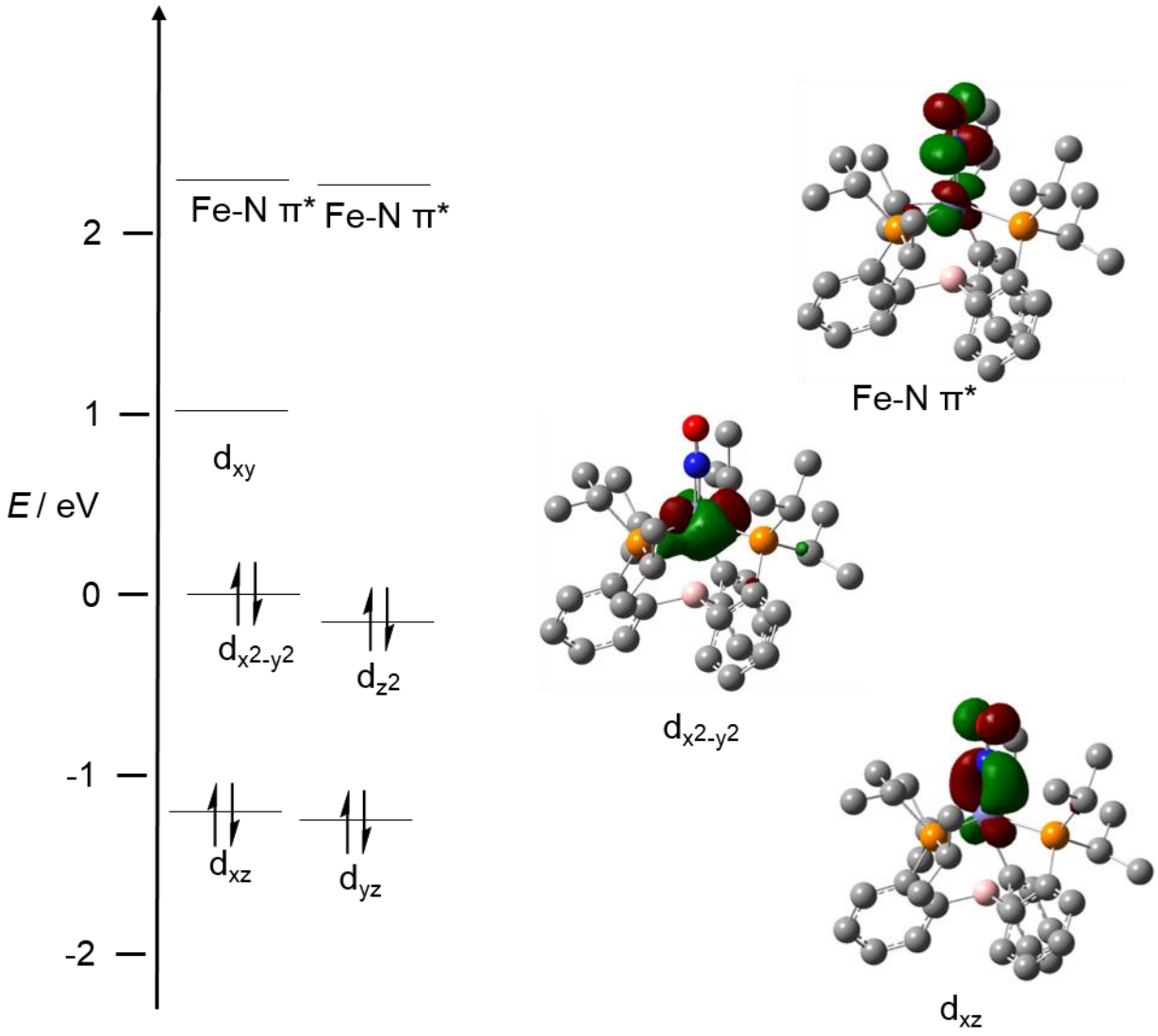


Figure S59: The gas-phase optimized geometry of $[TPBFeN_2]^-$ with hydrogens omitted.

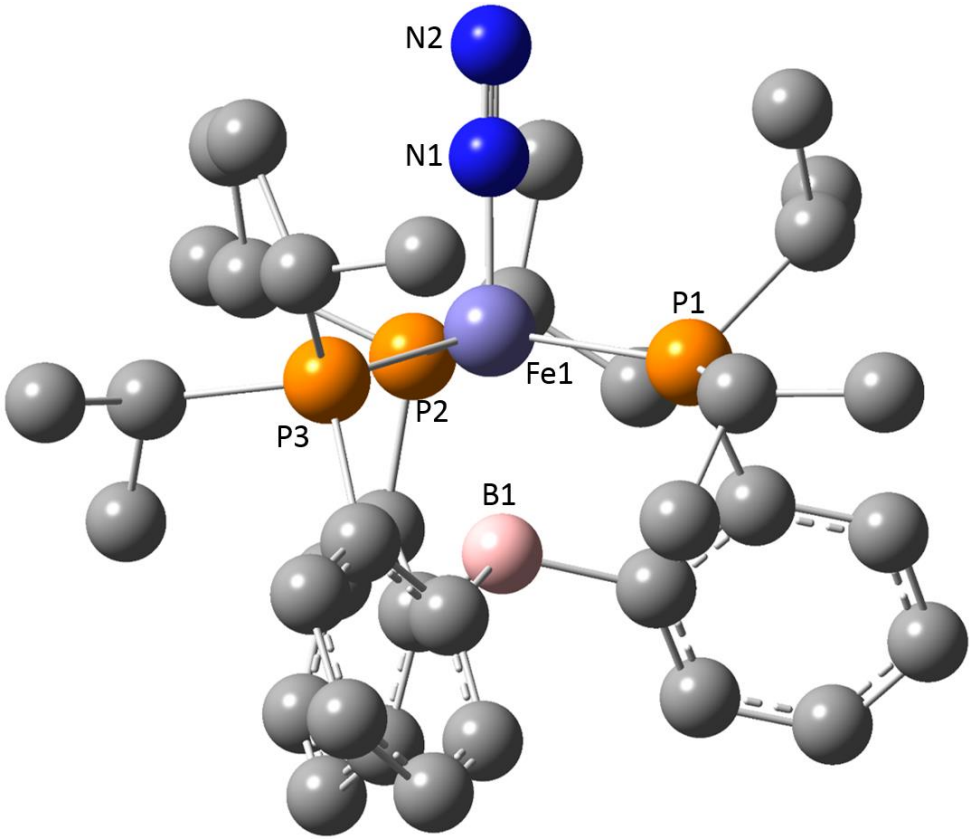


Table S28: Optimized coordinates for **$[TPBFeN_2]^-$**.

Fe	-0.04082507	-0.06063943	-0.95120745
P	2.19025707	-0.63009133	-0.69705167
P	-1.98847647	-1.10519294	-0.57654897
P	-0.37680571	2.10556226	-0.49346542
N	-0.08616632	-0.07355753	-2.73883112
C	0.40486161	2.45100586	1.14107663
C	0.58972285	1.26755480	1.91514790
C	2.19154265	-1.68543156	0.80908184
C	-2.10337944	2.94525684	-0.24691943
C	-1.67756710	-0.36088018	3.39069721
C	-1.38429843	-0.53456261	2.01241090
C	1.01428077	-2.21040125	2.84923963
C	2.87867334	-1.78838208	-2.04044996
C	1.10831437	-1.39180114	1.69192568
C	-3.56208813	-1.68125823	1.81331311
C	-3.32773692	0.26996266	-2.72946221
C	3.77785477	0.44638416	-0.47374141
C	0.37565477	3.40876492	-1.65833410
C	2.98026310	-3.51037789	2.23592616
C	3.11123275	-2.72095126	1.08127047
C	-2.77912298	2.46562595	1.05026882

C	3.73938685	1.28489464	0.81341404
C	-2.39158429	-1.15371519	1.22377222
C	0.82293596	3.71275762	1.61493681
C	-4.85955271	-1.21302659	-1.39056865
C	1.44426346	3.83363692	2.87055460
C	-2.20209104	-2.93980368	-1.02269741
B	0.06573800	-0.17072483	1.34579525
C	-3.58536111	-0.34487241	-1.34024742
C	-2.86544418	-0.83310683	3.97180839
C	1.63522505	2.68328730	3.65394471
C	1.92311609	-3.24697802	3.12138956
C	-2.07264157	-3.20822054	-2.53265279
C	1.93825018	-2.96640473	-2.33368576
C	1.21234686	1.42940752	3.17891083
C	-2.14619454	4.48827128	-0.26075385
C	1.87641452	3.18258657	-1.88931152
N	-0.11428063	-0.11822382	-3.88612359
C	5.12261002	-0.31059330	-0.51459752
C	-1.22297103	-3.80688180	-0.21152471
C	-0.36522354	3.42052698	-3.01165234
C	-3.80384133	-1.52507553	3.18713246
C	3.21401425	-1.02406968	-3.33788223
H	-1.52822250	4.90945805	0.55356400
H	3.74318703	1.13734927	-1.33751670
H	5.94867942	0.41057880	-0.35118087
H	5.32019264	-0.81896975	-1.47304080
H	5.18287986	-1.05919957	0.29610289
H	4.64345234	1.92441827	0.86820303
H	2.85512274	1.93350326	0.87290069
H	3.73114901	0.63566581	1.70654847
H	3.91919481	-2.94388324	0.37320197
H	3.68428561	-4.33003567	2.42903113
H	1.79896976	-3.85944199	4.02523960
H	0.18728913	-2.04115579	3.55039785
H	3.81780083	-2.21292232	-1.63636101
H	3.93337672	-0.20233495	-3.17282857
H	3.66524549	-1.71622279	-4.07714532
H	2.30596200	-0.59592438	-3.79385328
H	1.75134033	-3.56970973	-1.42886179
H	2.38692362	-3.63042922	-3.10002041
H	0.96801180	-2.61194196	-2.71879936
H	-1.09183262	-2.87888322	-2.91513186
H	-2.17106005	-4.29273072	-2.74078692
H	-2.84434416	-2.68280677	-3.12178584
H	-3.23161350	-3.20540137	-0.70707918
H	-1.35213664	-4.87710967	-0.47062006
H	-0.17601444	-3.52824744	-0.41853342
H	-1.38211093	-3.69100456	0.87359040
H	-0.95073759	0.16410172	4.02450695
H	-3.05399238	-0.67665057	5.04289069
H	-4.72319240	-1.92376294	3.63511436

H	-4.29527875	-2.22534562	1.20658945
H	-4.74286899	-2.08233333	-2.06305778
H	-5.70136542	-0.61019548	-1.78790195
H	-5.16735504	-1.58423868	-0.39993808
H	-3.78146856	0.48906038	-0.63939186
H	-4.21683213	0.84555840	-3.05826602
H	-2.45661320	0.94270152	-2.71908995
H	-3.12989520	-0.50131904	-3.49502670
H	-2.69614430	2.57550118	-1.10685487
H	-1.81447519	4.93538664	-1.21273920
H	-3.18684292	4.82883963	-0.08349886
H	-3.82697587	2.82622188	1.08985230
H	-2.78596268	1.37111020	1.15121681
H	-2.25101357	2.86572821	1.93445726
H	0.69762028	4.60798537	0.99208771
H	1.78823377	4.81407984	3.22474924
H	2.12973947	2.76248845	4.63193288
H	1.40363942	0.53782960	3.79219668
H	0.25215384	4.39846733	-1.17647614
H	0.03294949	4.22752272	-3.65955655
H	-0.22546193	2.46376278	-3.54293247
H	-1.45190771	3.58641456	-2.90448163
H	2.44734389	3.23027707	-0.94650905
H	2.28100253	3.95469676	-2.57485816
H	2.05004468	2.19326490	-2.34760203

Figure S60: The gas-phase optimized geometry of $[TPBFeNAd]^+$ with hydrogens omitted.

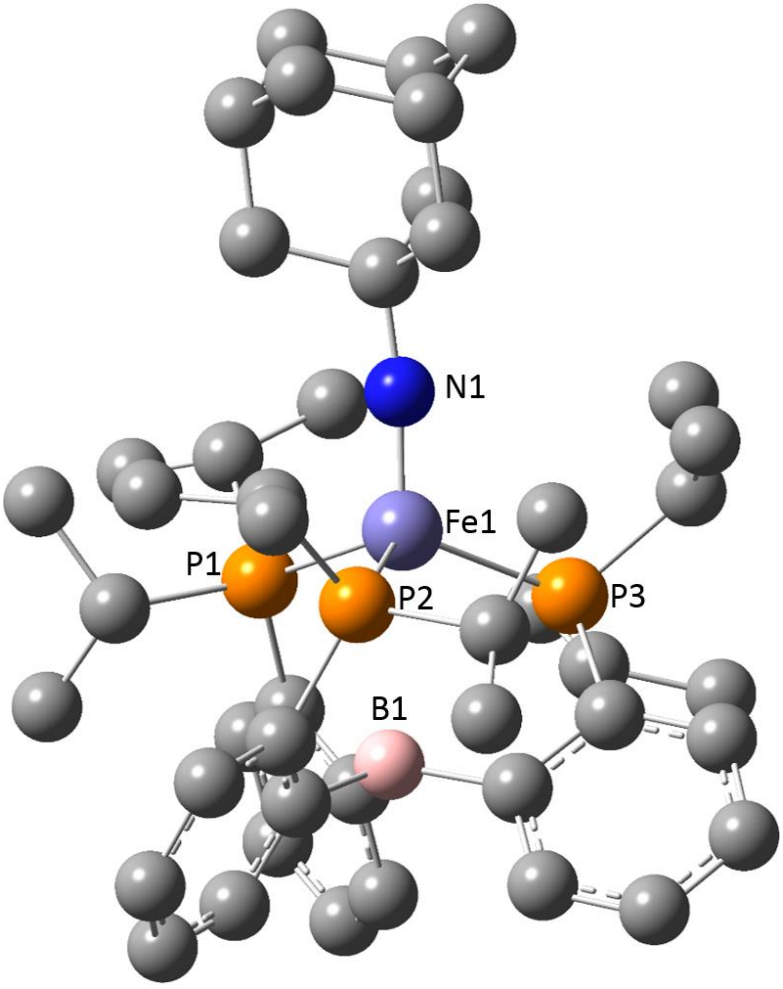


Table S29: Optimized coordinates for **$[TPBFeNAd]^+$**

Fe	0.29655900	-0.13445000	0.15345400
P	-0.45470300	-0.98486000	-1.84602600
P	-0.13211600	2.21135100	0.19861100
P	-0.77314200	-1.55840000	1.75623700
N	1.94046700	-0.20655400	0.19490900
C	-1.97062800	-0.38044900	2.48446200
C	-0.33433600	2.74907700	2.00302500
C	5.49341700	-1.58260800	0.28753200
C	3.37015400	-0.17056000	0.09220700
C	-2.68432400	0.38969600	1.52165900
C	-1.65647900	2.70044500	-0.68803100
C	0.77171500	-2.27456600	-2.49983900
C	-2.96226500	-1.01832700	-0.82507800
C	-3.77365200	1.91727500	-1.57566800
C	3.94865200	-1.59720800	0.39453300
C	5.53290700	0.82770000	1.01950000
C	3.98820600	0.82264700	1.13261000

C	0.37324600	-2.04118600	3.16672200
B	-2.42148800	0.26650900	-0.05235100
C	-3.67492500	1.27957000	2.00761100
C	-3.95080800	1.39967800	3.37950400
C	-1.90553200	3.97597400	-1.23647800
C	-3.21694000	0.64956300	4.31241400
C	-3.08691300	4.21888500	-1.95629700
C	5.37300400	0.25571100	-1.43382900
C	3.82761300	0.25048300	-1.34100600
C	-4.01864600	3.18487100	-2.13125000
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C	-4.30686500	-1.43841500	-0.68724900
C	5.91326300	-1.16272900	-1.13944900
C	-2.14566500	-1.69172600	-1.76747700
C	-0.53637100	0.27256300	-3.27986000
C	-1.91512300	-3.07665800	1.58495900
C	-2.66720000	-2.73932600	-2.55557300
C	-4.82293300	-2.49335900	-1.45915200
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C	5.94883000	1.25776900	-0.40632000
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C	-4.00268700	-3.14327100	-2.39499400
C	1.20607300	-0.86292600	3.69213500
C	0.45044700	-2.94103500	-3.86102200
C	1.38515200	3.15665200	-2.01667200
C	-2.22655200	-0.24002800	3.86406300
C	0.76782700	0.39904200	-4.09701600
C	1.18205800	-3.36402600	-1.49401600
C	1.00178600	2.75368100	2.77290100
C	-1.74541300	0.09003300	-4.22054200
C	-1.13969300	4.04956000	2.19835000
C	-1.43675900	-4.21001200	0.66379900
C	1.37618700	4.75034800	-0.06611200
C	-2.35929100	-3.63015600	2.95527000
C	-2.59851300	1.64838400	-0.83554200
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H	5.93206300	1.54664400	1.76026400
H	7.05215600	1.28902000	-0.48509100
H	5.65967800	0.56190800	-2.45806900
H	3.42404500	1.25307400	-1.57187100
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H	0.69379200	-4.16361100	2.63301200
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H	-1.65797000	-0.81611200	4.60195900
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H	-4.72866200	2.09129500	3.72211000
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H	1.35414800	-2.96039600	-0.48354200
H	0.41918800	-4.15580700	-1.42615100
H	1.39466200	-3.27323800	-4.33112100
H	-0.06216900	-2.28319800	-4.57907600
H	-0.16757000	-3.84461800	-3.72458400
H	-2.04525400	-3.25033900	-3.29344100
H	-4.39744600	-3.96702400	-2.99943500
H	-5.86374100	-2.81013200	-1.32738000
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H	-1.71310200	-0.86691200	-4.77011900
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H	-1.18541500	4.78858600	-1.11337300
H	-3.26862100	5.20986600	-2.38584500
H	-4.93613700	3.36312100	-2.70335300
H	-4.51227900	1.11865900	-1.71518100
H	2.16261300	2.74792400	-0.05132800
H	2.30164700	3.66691000	-2.36624700
H	1.43194300	2.11128400	-2.35058000
H	0.52586500	3.63755000	-2.51511500
H	2.33156900	5.15523300	-0.44958800
H	1.36989700	4.90526300	1.02187000
H	0.57420700	5.36749100	-0.50284400
H	1.65403400	3.59858300	2.49674000
H	1.56898000	1.82130100	2.61925300
H	0.79291900	2.84715600	3.85440500
H	-0.94535500	1.92983300	2.41633100
H	-1.30264800	4.20182800	3.28139800

H	-2.12842200	3.99339400	1.71541600
H	-0.61966600	4.94190400	1.81361200

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